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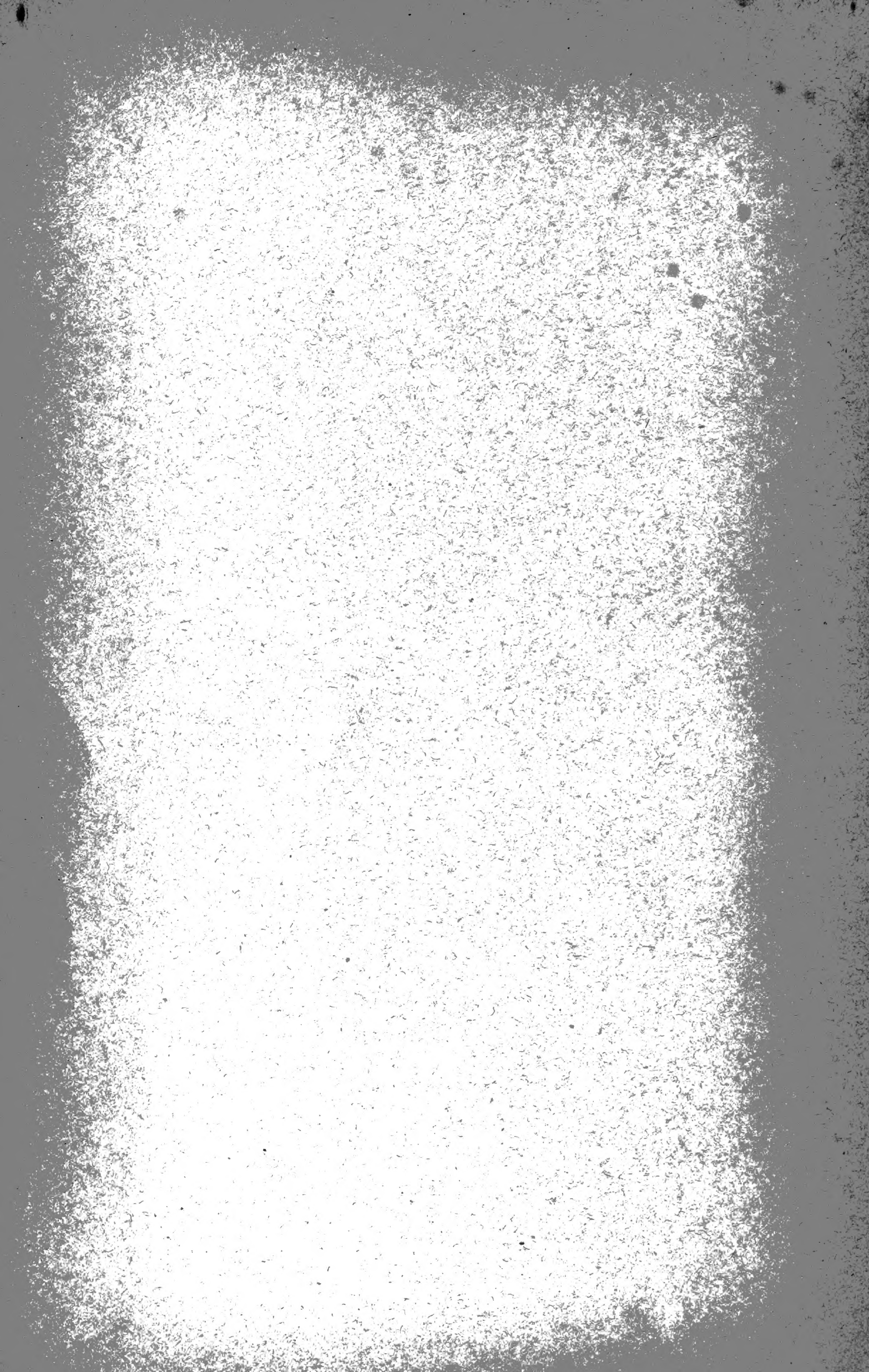
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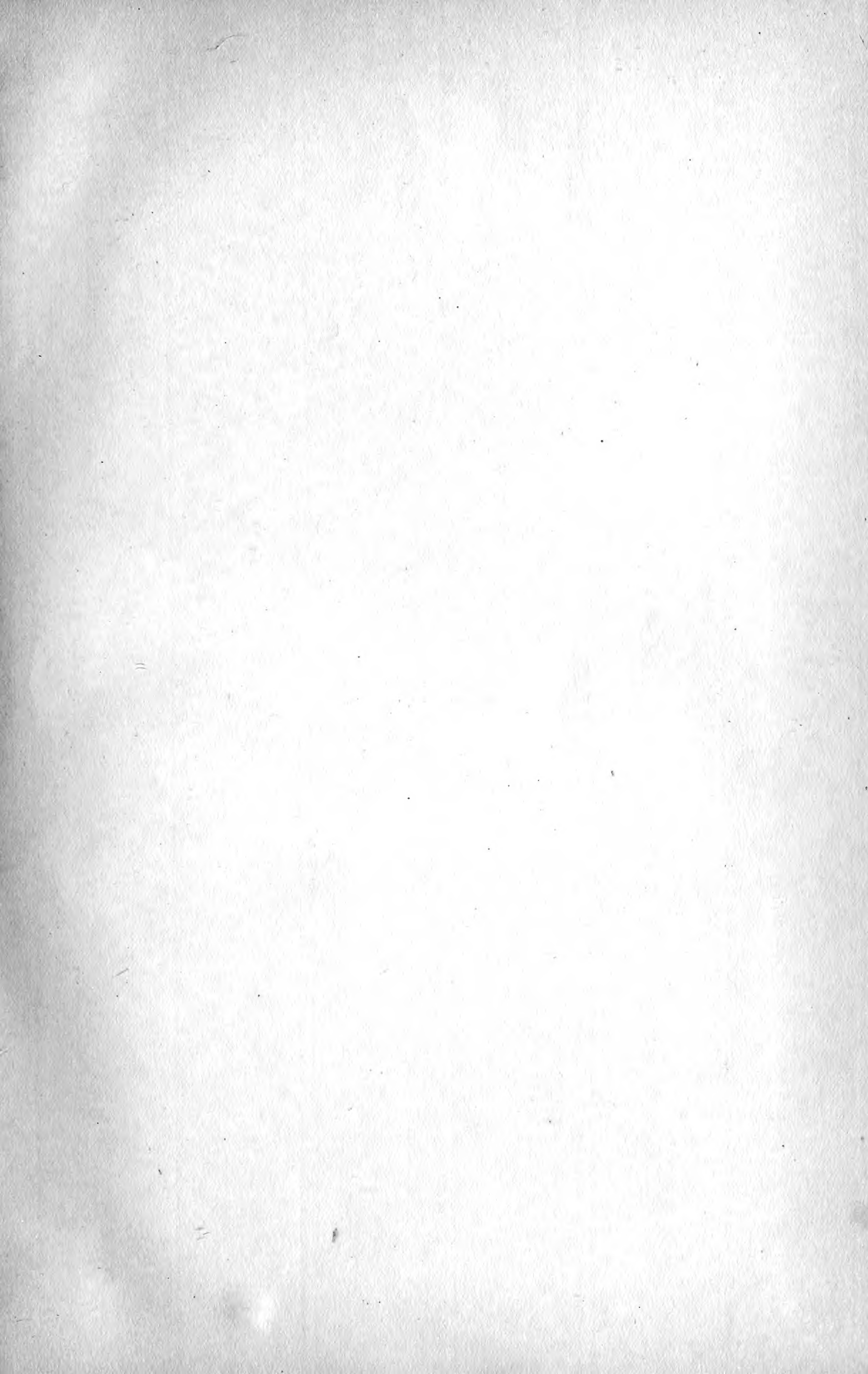
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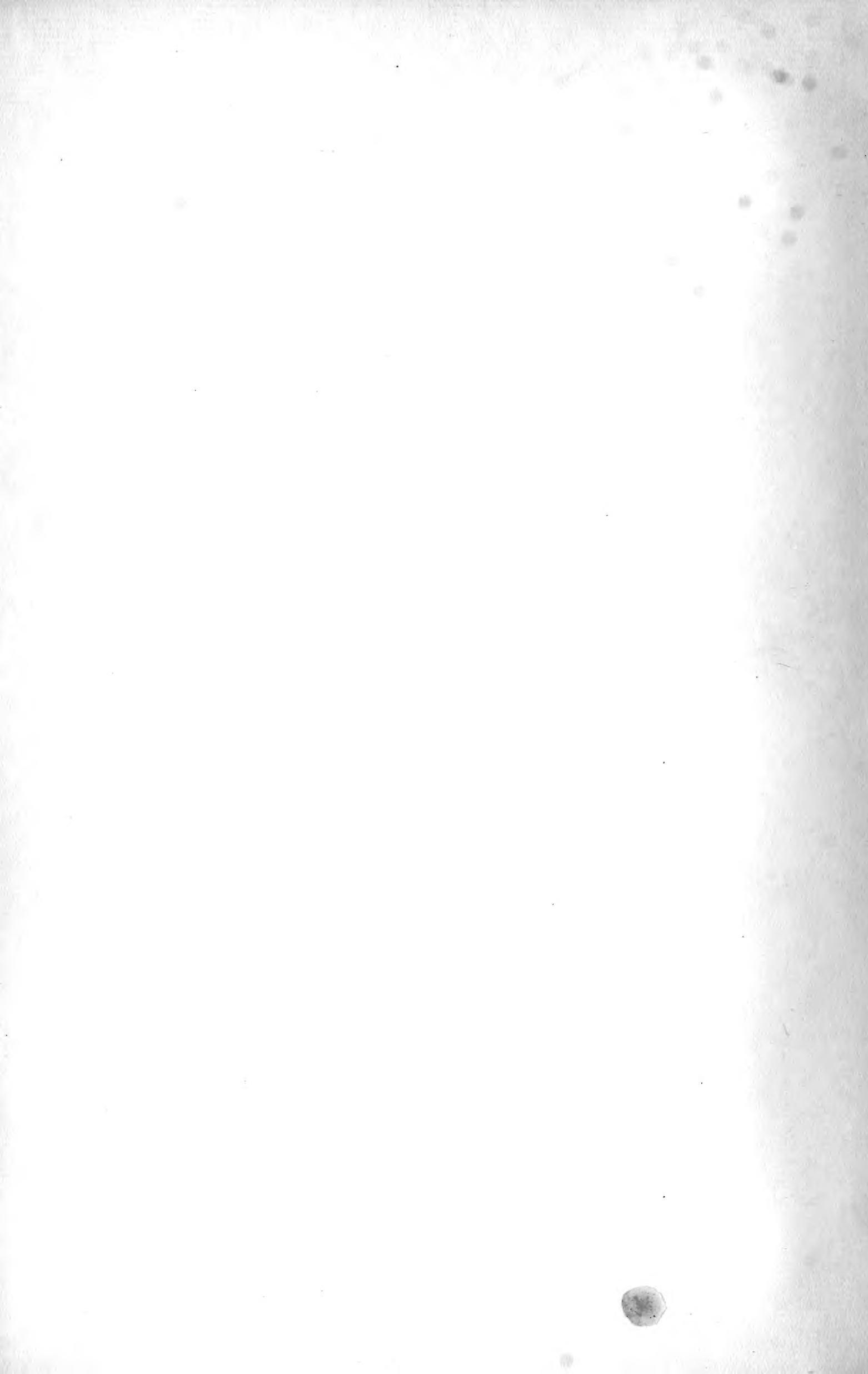
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VOLUME XV

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JOHANNES MÜLLER. — AMSTERDAM  
:=====: AUGUST 1913 :=====:

14/62833 Jan 6<sup>th</sup>

(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling van 25 Mei 1912 tot 25 April 1913 Dl. XXI.)



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VOLUME XV  
( — 1<sup>ST</sup> PART — )

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PROCEEDINGS OF THE MEETING  
of Saturday May 25, 1912.

*President:* Prof. H. A. LORENTZ.

*Secretary:* Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeeling van Zaterdag 25 Mei 1912, Dl. XXI).

C O N T E N T S.

- M. J. VAN UVEN "Homogeneous linear differential equations of order two with given relation between two particular integrals" (5th Communication). (Communicated by Prof. W. KAPTEYN), p. 2.
- J. W. LE HEUX: "On some internal unsaturated ethers". (Communicated by Prof. P. VAN ROMBURGH), p. 19.
- E. H. BÜCHNER: "The radioactivity of rubidium and potassium compounds". II. (Communicated by Prof. A. F. HOLLEMAN), p. 22.
- J. C. KLUYVER: "On a differential equation of SCHÄFLI", p. 27.
- T. VAN LOHUIZEN: "Series in the spectra of Tin and Antimony". (Communicated by Prof. P. ZEEMAN), p. 31. (With one plate).
- W. KAPTEYN: "New researches upon the centra of the integrals which satisfy differential equations of the first order and the first degree" (2nd part), p. 46.
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- L. S. ORNSTEIN: "Accidental deviations of density in mixtures". (Communicated by Prof. H. A. LORENTZ), p. 54.
- G. DE VRIES: "Calculus ratioum" (2nd Part). (Communicated by Prof. JAN DE VRIES), p. 64.
- E. W. ROSENBERG: "Contribution to the knowledge of the development of the vertebral column of man", p. 80.
- PH. KOHNSTAMM: "On vapour-pressure lines of binary systems with widely divergent values of the vapour-pressures of the components." (In connection with experiments of Mr. KATZ) (Communicated by Prof. J. D. VAN DER WAALS), p. 96.
- L. E. J. BROUWER: "On looping coefficients". (Communicated by Prof. D. J. KORTEWEG), p. 113.

**Mathematics.** — “Homogeneous linear differential equations of order two with given relation between two particular integrals.”  
 By Dr. M. J. VAN UVEN. (Communicated by Prof. W. KAPTEYN).  
 (5<sup>th</sup> communication).

(Communicated in the meeting of April 26, 1912).

The equations (8) and (29) (see 1<sup>st</sup> comm. p. 393 and 398) show us in the case that the equation  $F(x, y, z) = 0$  represents a conic (see for the notation: 4<sup>th</sup> comm. p. 1015):

$$q_1 = \frac{c^2 z^3 H}{(n-1)^2 F_z^3} = \frac{\Delta z^3}{g^3} = e^{\int 1d\tau},$$

where  $c$  is put equal to 1.

From this ensues

$$\frac{\dot{g}}{g} = -\frac{I}{3}.$$

Let us further put:

$$g = a_{33} \zeta^2 z, \quad \dots \dots \dots (72)$$

we then find:

$$\frac{\dot{\zeta}}{\zeta} = \frac{1}{2} \frac{\dot{g}}{g} = -\frac{I}{6},$$

or

$$I = -6 \frac{\dot{\zeta}}{\zeta} \dots \dots \dots (73)$$

The equation (62) (see 4<sup>th</sup> comm. p. 1015) runs now as follows:

$$I^2 = 36 \frac{\dot{\zeta}^2}{\zeta^2} = \frac{9}{a_{33} \Delta z^2 \zeta^2} (-a_{33}^2 A_{33} z^2 \zeta^4 + 2a_{33} \Delta z^2 \zeta^2 - a_{33} \Delta z^2),$$

or making use of the notation (59) (4<sup>th</sup> comm. p. 1003),

$$4\dot{\zeta}^2 = -\lambda^2 \zeta^4 + 2\zeta^2 - 1; \quad \dots \dots \dots (74)$$

so  $\zeta'$  is likewise an elliptic function of  $\tau$ . Its invariant has the same value (68) as that of the function  $u = I^2$  (compare (67)<sup>1)</sup> (4<sup>th</sup> comm. p. 1006).

We can now deduce out of the equation

$$A_{23}x - A_{13}y = \sqrt{-A_{33}g^2 + 2\Delta gz - \Delta a_{33}z^2} = \sqrt{a_{33}\Delta} \cdot z \sqrt{-\lambda^2 \zeta^4 + 2\zeta^2 - 1} \quad (75)$$

(see 4<sup>th</sup> comm. p. 1005 at the bottom)

$$A_{23}x - A_{13}y = 2z\sqrt{a_{33}\Delta} \cdot \dot{\zeta} \dots \dots \dots (76)$$

<sup>1)</sup> In the 4<sup>th</sup> comm. in the table on p. 1014 and in the enumeration of the cases on p. 1015  $\delta_1 = e^{i\psi}$  and  $\delta_2 = e^{-i\psi}$  must be replaced by  $\delta_1 = e^{-i\psi}$ ,  $\delta_2 = e^{+i\psi}$ .

As from (73) follows

$$a_{13}x + a_{23}y = a_{33}z (\zeta^2 - 1), \dots \dots \dots (77)$$

we find with the aid of (76) and (77)

$$\left. \begin{aligned} (a_{13}A_{13} + a_{23}A_{23})x &= (\Delta - a_{33}A_{33})x = \Delta(1 - \lambda^2)x = \\ &= \{2a_{23}\sqrt{a_{33}\Delta} \cdot \dot{\zeta} + a_{33}A_{13}(\zeta^2 - 1)\}z, \\ (a_{13}A_{13} + a_{23}A_{23})y &= (\Delta - a_{33}A_{33})y = \Delta(1 - \lambda^2)y = \\ &= \{-2a_{13}\sqrt{a_{33}\Delta} \cdot \dot{\zeta} + a_{33}A_{23}(\zeta^2 - 1)\}z. \end{aligned} \right\} (78)$$

In this way we have expressed  $x$  and  $y$  as functions of  $\tau$  with the aid of the function  $\zeta$ . It is now still our task to determine  $\zeta$  as function of  $\tau$ . Let us now put in

$$9\dot{u}^2 = u^3 - 36u^2 + 324(1 - \lambda^2)u$$

(see 4<sup>th</sup> comm. p. 1016)

$$u = I^2 = 36v + 12, \dots \dots \dots (79)$$

we then find

$$\dot{v}^2 = 4v^3 - \frac{1 + 3\lambda^2}{3}v - \frac{9\lambda^2 - 1}{27}.$$

By applying the ordinary notation

$$\frac{1 + 3\lambda^2}{3} = g_2, \quad \frac{9\lambda^2 - 1}{27} = g_3, \dots \dots \dots (80)$$

we then find

$$v = p(\tau; g_2, g_3)$$

and

$$I = \pm 6 \sqrt{p(\tau; g_2, g_3) + \frac{1}{3}}, \dots \dots \dots (81)$$

so that

$$\frac{\dot{\zeta}}{\zeta} = \mp \sqrt{p(\tau; g_2, g_3) + \frac{1}{3}} \dots \dots \dots (82)$$

Before transforming the  $p$ -function of WEIERSTRASS we wish to remind the readers that the roots of  $\dot{u} = 0$  are

$$u_1 = 0, \quad u_2 = 18(1 + \lambda), \quad u_3 = 18(1 - \lambda),$$

so that for the roots of  $\dot{v} = 0$  (see (79)) we find

$$v_1 = -\frac{1}{3}, \quad v_2 = \frac{1 + 3\lambda}{6}, \quad v_3 = \frac{1 - 3\lambda}{6}.$$

We shall now investigate the relative value of these roots in the three cases: II ( $+1 < \lambda < +\infty$ ), IV ( $+1 > \lambda > 0$ ), VI ( $\lambda = i\lambda'$ ) (see 4<sup>th</sup> comm. p. 1014).

Case II:  $+1 < \lambda < +\infty$

$$v_1 = -\frac{1}{3}, \quad v_2 > \frac{2}{3}, \quad v_3 < -\frac{1}{3}.$$

The roots are all real. Let us call them in the ordinary way in descending order  $e_1, e_2, e_3$ , we then find

$$e_1 = \frac{1+3\lambda}{6}, \quad e_2 = -\frac{1}{3}, \quad e_3 = \frac{1-3\lambda}{6}. \quad \dots \quad II$$

Case IV:  $+1 > \lambda > 0$ .

$$v_1 = -\frac{1}{3}, \quad \frac{2}{3} > v_2 > \frac{1}{6}, \quad \frac{1}{6} > v_3 > -\frac{1}{3}.$$

The roots are here, too, all real and run when arranged:

$$e_1 = \frac{1+3\lambda}{6}, \quad e_2 = \frac{1-3\lambda}{6}, \quad e_3 = -\frac{1}{3}. \quad \dots \quad IV$$

Case VI:  $\lambda = i\lambda'$ .

The roots  $v_2$  and  $v_3$  are now conjugate complex. If we follow the notation generally assumed, we then write:

$$e_2' = -\frac{1}{3}, \quad e_1' = \frac{1+3i\lambda'}{6}, \quad e_3' = \frac{1-3i\lambda'}{6}. \quad \dots \quad VI$$

When reducing the  $p$ -functions to the elliptic functions of JACOBI we make use of the following formulae of reduction:<sup>1)</sup>

$$sn(v) = \sqrt{\frac{e_1 - e_3}{p(\tau) - e_3}}, \quad cn(v) = \sqrt{\frac{p(\tau) - e_1}{p(\tau) - e_3}}, \quad dn(v) = \sqrt{\frac{p(\tau) - e_2}{p(\tau) - e_3}},$$

$$v = \tau \sqrt{e_1 - e_3}, \quad k^2 = \frac{e_2 - e_3}{e_1 - e_3}, \quad k'^2 = \frac{e_1 - e_2}{e_1 - e_3};$$

$$p(\tau; e_1', e_2', e_3') = e_2' + \frac{e_1' - e_3'}{4ikk'} \cdot \frac{cn^2(v)}{sn^2(v) \cdot dn^2(v)},$$

$$v = \tau \sqrt{(e_2' - e_3')(e_2' - e_1')}, \quad k^2 = \frac{-3e_2' + 2\sqrt{(e_2' - e_3')(e_2' - e_1')}}{4\sqrt{(e_2' - e_3')(e_2' - e_1')}}},$$

$$k'^2 = \frac{+3e_2' + 2\sqrt{(e_2' - e_3')(e_2' - e_1')}}{4\sqrt{(e_2' - e_3')(e_2' - e_1')}}}, \quad kk' = \frac{\sqrt{-9e_2'^2 + 4(e_2' - e_3')(e_2' - e_1')}}{4\sqrt{(e_2' - e_3')(e_2' - e_1')}}}.$$

The expression for  $\zeta: \zeta$  becomes in this way:

in case II

$$\frac{\dot{\zeta}}{\zeta} = \mp \sqrt{p(\tau; g_2, g_3) - e_2} = \mp \sqrt{e_1 - e_3} \cdot \frac{dn(v)}{sn(v)} \left. \vphantom{\frac{\dot{\zeta}}{\zeta}} \right\} v = \tau \sqrt{e_1 - e_3},$$

in case IV

$$\frac{\dot{\zeta}}{\zeta} = \mp \sqrt{p(\tau; g_2, g_3) - e_3} = \pm \sqrt{e_1 - e_3} \cdot \frac{1}{sn(v)} \left. \vphantom{\frac{\dot{\zeta}}{\zeta}} \right\} \begin{matrix} k^2 = \frac{e_2 - e_3}{e_1 - e_3} \\ k'^2 = \frac{e_1 - e_2}{e_1 - e_3} \end{matrix}$$

<sup>1)</sup> See i. a. M. KRAUSE: Theorie der elliptischen Funktionen (Leipzig, TEUBNER (p. 135, 136, 147, 148).



in case VI

$$\frac{\zeta}{\bar{\zeta}} = \mp \sqrt{p(\tau; e_1', e_2', e_3') - e_2'} = \mp \sqrt{\frac{e_1' - e_3'}{4 i k k'} \cdot \frac{cn(v)}{sn(v) \cdot dn(v)},}$$

$$v = \tau \sqrt{(e_2' - e_3')(e_2' - e_1')}, \quad k k' = \frac{\sqrt{-9e_2'^2 + 4(e_2' - e_3')(e_2' - e_1')}}{\sqrt{(e_2' - e_3')(e_2' - e_1')}},$$

or, after having expressed the roots  $e_1, e_2, e_3, e_1', e_2', e_3'$  in  $\lambda$ :

in case II

$$\frac{\zeta}{\bar{\zeta}} = \mp \sqrt{\lambda} \cdot \frac{dn(v)}{sn(v)}; \quad v = \tau \sqrt{\lambda}, \quad k^2 = \frac{\lambda - 1}{2\lambda}, \quad k'^2 = \frac{\lambda + 1}{2\lambda};$$

in case IV

$$\frac{\zeta}{\bar{\zeta}} = \mp \sqrt{\frac{1 + \lambda}{2}} \cdot \frac{1}{sn(v)}; \quad v = \tau \sqrt{\frac{1 + \lambda}{2}}, \quad k^2 = \frac{1 - \lambda}{1 + \lambda}, \quad k'^2 = \frac{2\lambda}{1 + \lambda}; \quad \left. \vphantom{\frac{\zeta}{\bar{\zeta}}} \right\} (83)$$

in case VI

$$\frac{\zeta}{\bar{\zeta}} = \mp \sqrt{\frac{\sqrt{1 + \lambda'^2}}{2}} \cdot \frac{cn(v)}{sn(v) \cdot dn(v)}; \quad v = \tau \sqrt{\frac{\sqrt{1 + \lambda'^2}}{2}};$$

$$k^2 = \frac{1 + \sqrt{1 + \lambda'^2}}{2\sqrt{1 + \lambda'^2}}, \quad k'^2 = \frac{-1 + \sqrt{1 + \lambda'^2}}{2\sqrt{1 + \lambda'^2}}.$$

Let us substitute these expressions in (14), we then find successively

$$\text{in case II} \quad \zeta_1 = \pm \frac{i}{\sqrt{\lambda}} \cdot \frac{1 + cn(v)}{sn(v)}, \quad \zeta_2 = \pm \frac{1}{\lambda \zeta_1},$$

$$\text{in case IV} \quad \zeta_1 = \pm \frac{i}{\lambda} \sqrt{\frac{1 + \lambda}{2}} \cdot \frac{cn(v) + dn(v)}{sn(v)}, \quad \zeta_2 = \pm \frac{1}{\lambda \zeta_1},$$

$$\text{in case VI} \quad \zeta_1 = \pm \frac{\sqrt[4]{4(1 + \lambda'^2)}}{\lambda'} \cdot \frac{dn(v)}{sn(v)}, \quad \zeta_2 = \pm \frac{i}{\lambda' \zeta_1}.$$

Let us now choose

$$l = + 6 \sqrt{p(\tau; g_2, g_3) + \frac{1}{3}}$$

and for  $\zeta$  the expressions  $\zeta_1$  with the upper sign, we find:

$$\begin{aligned}
II \quad I &= +6\sqrt{\lambda} \cdot \frac{dn(v)}{sn(v)} ; v = \tau\sqrt{\lambda} , k^2 = \frac{\lambda-1}{2\lambda} , k'^2 = \frac{\lambda+1}{2\lambda} ; \\
\zeta &= \frac{+i}{\sqrt{\lambda}} \cdot \frac{1+cn(v)}{sn(v)} , \dot{\zeta} = -i \cdot \frac{\{1+cn(v)\}dn(v)}{sn^2(v)} . \\
IV \quad I &= +6 \sqrt{\frac{1+\lambda}{2}} \cdot \frac{1}{sn(v)} ; v = \tau \sqrt{\frac{1+\lambda}{2}} , \\
k^2 &= \frac{1-\lambda}{1+\lambda} , k'^2 = \frac{2\lambda}{1+\lambda} ; \\
\zeta &= + \frac{i}{\lambda} \sqrt{\frac{1+\lambda}{2}} \cdot \frac{cn(v)+dn(v)}{sn(v)} , \dot{\zeta} = \frac{-i(1+\lambda)}{2\lambda} \cdot \frac{cn(v)+dn(v)}{sn^2(v)} . \\
VI \quad I &= +6 \sqrt{\frac{\sqrt{1+\lambda'^2}}{2}} \cdot \frac{cn(v)}{sn(v) \cdot dn(v)} , v = \sqrt{\frac{\sqrt{1+\lambda'^2}}{2}} , \\
k^2 &= \frac{1+\sqrt{1+\lambda'^2}}{2\sqrt{1+\lambda'^2}} , k'^2 = \frac{-1+\sqrt{1+\lambda'^2}}{2\sqrt{1+\lambda'^2}} \\
\zeta &= \frac{\sqrt{4(1+\lambda'^2)}}{\lambda'} \cdot \frac{dn(v)}{sn(v)} , \dot{\zeta} = - \frac{\sqrt{1+\lambda'^2}}{\lambda'} \cdot \frac{cn(v)}{sn^2(v)} .
\end{aligned} \tag{84}$$

Let us restrict ourselves to real points  $(x, y)$  of the conic, then follows from (78) that  $\sqrt{a_{33}\Delta} \cdot \dot{\zeta}$  must always be real.

Case II (in which  $\lambda$  is real) appears only with the hyperbola for which holds  $A_{33} < 0$ ; so we have here

$$a_{33}\Delta = \frac{a_{33}A_{33}}{\Delta} \cdot \frac{\Delta^2}{A_{33}} = \frac{\lambda^2\Delta^2}{A_{33}} < 0.$$

From this ensues that in case II we shall find  $\dot{\zeta}$  always imaginary, and therefore  $\frac{\{1+cn(v)\}dn(v)}{sn^2(v)}$  is real;

Case IV is found with the hyperbola as well as with the ellipse. As here too  $\lambda$  is real we find

IVa. with the hyperbola ( $A_{33} < 0$ )  $a_{33}\Delta < 0$ , so  $\dot{\zeta}$  is imaginary or  $\frac{cn(v)+dn(v)}{sn^2(v)}$  real;

IVb. with the ellipse ( $A_{33} > 0$ )  $a_{33} > 0$ , so  $\zeta$  is real and  $\frac{cn(v)+dn(v)}{sn^2(v)}$

is purely imaginary.

Also case VI appears with the hyperbola as well as with the ellipse. On account of  $\lambda$  being purely imaginary, thus  $\lambda^2$  negative, holds:

VIa. for the hyperbola ( $A_{33} < 0$ )  $a_{33}\Delta > 0$ , hence  $\dot{\zeta}$  real, and  $\frac{cn(v)}{sn^2(v)}$  real;

VIb. for the ellipse ( $A_{33} > 0$ )  $a_{33}\Delta < 0$ , thus  $\zeta$  purely imaginary and also  $\frac{cn(v)}{sn^2(v)}$  purely imaginary.

From the preceding we see that  $v$  must move in its complex plane on the sides of the rectangles of the net formed by the lines  $v = mK +$  purely imaginary and  $v = niK' +$  real.

The value of  $\zeta^2 = \frac{g}{a_{33}} = \frac{a_{13}x + a_{23}y}{a_{33}} + 1$  is evidently positive on that side of the polar line  $g = 0$  of  $O$  with respect to the conic where  $O$  lies itself; on the other side  $\zeta^2$  is negative. The polar line  $g = 0$  of  $O$  divides therefore the plane into two parts: in one (in which  $O$  lies)  $\zeta$  is real, in the other  $\zeta$  is imaginary.

In the points of contact  $R_1$  and  $R_2$  of the tangents out of  $O$  to the conic  $\zeta$  is 0, so  $I = \infty$ .

In the points at infinity  $S_1$  and  $S_2$  we find that  $\zeta$  and  $\zeta'$  are both infinite and  $I$  is also equal to  $\infty$ .

The diameter passing through  $O$  ( $A_{23}x - A_{13}y = 0$ ) intersects the conic in two points  $T_1$  and  $T_2$ , for which  $\zeta = 0$ , thus  $I = 0$ .

If we substitute the expressions (84) for  $\zeta$  and  $\zeta'$  in the formulae (78) we at last arrive at  $x$  and  $y$  as functions of  $\tau$ .

With a view to  $\sqrt{A_{33}}$  being real or not, we shall deal with the cases of IV and VI separately. Farthermore we shall express  $\lambda$  everywhere

in  $\sigma = \frac{1-\lambda}{1+\lambda}$ , thus in the anharmonic ratio of the four points

$R_1, R_2, S_1, S_2$ . We shall give the formulae for  $x$  only. The expressions for  $y$  we can easily find by replacing  $a_{23}$  in those for  $x$  by  $-a_{13}$  and  $A_{23}$  by  $A_{13}$ .

We then find at last:

$$II \quad x = \frac{1-\sigma}{2\sigma} \cdot \frac{1+cn(v)}{sn^2(v)} \left[ - (1+\sigma) \frac{a_{23}}{\sqrt{-A_{33}}} dn(v) + \frac{A_{13}}{-A_{33}} \{1 + \sigma cn(v)\} \right],$$

$$v = \tau \sqrt{\frac{1-\sigma}{1+\sigma}};$$

$$IVa \quad x = \frac{1}{2\sigma} \cdot \frac{cn(v) + dn(v)}{sn^2(v)} \left[ - (1+\sigma) \frac{a_{23}}{\sqrt{-A_{33}}} + \frac{A_{13}}{-A_{33}} \{\sigma cn(v) + dn(v)\} \right],$$

$$v = \tau \sqrt{\frac{1}{1+\sigma}};$$

$$IVb \quad x = \frac{1}{2\sigma} \cdot \frac{cn(v) + dn(v)}{i sn^2(v)} \left[ - (1+\sigma) \frac{a_{23}}{\sqrt{-A_{33}}} - \frac{A_{13}}{A_{33}} i \{\sigma cn(v) + dn(v)\} \right],$$

$$v = \tau \sqrt{\frac{1}{1+\sigma}};$$

$$VIa \quad x = \frac{2 \operatorname{cn}(v)}{\operatorname{sn}^2(v)} \left[ \cos \frac{\psi}{2} \cdot \frac{a_{23}}{\sqrt{-A_{33}}} + 2 \cos^2 \frac{\psi}{4} \cdot \frac{A_{13}}{-A_{33}} \operatorname{cn}(v) \right],$$

$$v = \frac{\tau}{\sqrt{2 \cos \frac{\psi}{2}}}, \quad \sigma = e^{-i\psi}, \quad \psi = i \log \sigma;$$

$$VIb \quad x = \frac{2 \operatorname{cn}(v)}{i \operatorname{sn}^2(v)} \left[ \cos \frac{\psi}{2} \cdot \frac{a_{23}}{\sqrt{A_{33}}} - 2 \cos^2 \frac{\psi}{4} \cdot \frac{A_{13}}{A_{33}} i \operatorname{cn}(v) \right],$$

$$v = \frac{\tau}{\sqrt{2 \cos \frac{\psi}{2}}}, \quad \sigma = e^{-i\psi}, \quad \psi = i \log \sigma.$$

When point  $(x, y)$  describes the conic, the variable  $v$  will describe a certain curve in its complex plane. This curve we shall investigate in the five cases mentioned above whilst at the same time we shall indicate how the functions  $\zeta$ ,  $\dot{\zeta}$  and  $I$  bear themselves during that motion.

*Case II.* Point  $O$  lies in the domain of the conjugate hyperbola; the diameter through  $O$  does not intersect the curve, i.e. the points  $T_1$  and  $T_2$  are imaginary. On the contrary the points  $R_1, R_2, S_1, S_2$  are all real.

II	in $S_1^\infty$	on $S_1^\infty R_1$	in $R_1$	on $R_1 S_2^\infty$	in $S_2^\infty$	on $S_2^\infty R_2$	in $R_2$	on $R_2 S_1^\infty$	in $S_1^\infty$
$v$	0	purely imag.	$2iK'$	$2iK' + \text{real}$	$2K + 2iK'$	$2K + \text{p. imag}$	$2K$	real	0
$\zeta$	$\infty$	pos. real	0	pos. imag.	$\infty$	pos. real	0	pos. imag.	$\infty$
$\dot{\zeta}$		pos. imag.	$+\frac{i}{2}$	pos. imag.	$\infty$	neg. imag.	$-\frac{i}{2}$	neg. imag.	$\infty$
$I$	$\infty$	neg. imag.	$\infty$	neg. real	$\infty$	pos. imag.	$\infty$	pos. real	$\infty$

Here the curves are sketched which are described by  $v$  and  $I$  in their respective complex planes.

The points where  $I$  turns its direction of motion are arrived at by putting  $\dot{I} = 0$ . We then find the values of  $I$  corresponding to the roots of  $\dot{u} = 0$ ; these are  $u_1 = 0$ ,  $u_2 = \infty$ ,  $u_3 = 18(1+\lambda)$ ,  $u_4 = 18(1-\lambda)$ ; or  $I_1 = 0$ ,  $I_2 = \infty$ ,  $I_3 = 6 \sqrt{\frac{1+\lambda}{2}}$ ,

IVa	in $S_1^\infty$	on $S_1^\infty R_1$	in $R_1$	on $R_1 T_1$	in $T_1$	on $T_1 R_2$	in $R_2$	on $R_2 S_2^\infty$	in $S_2^\infty$	on $S_2^\infty T_2$	in $T_2$	on $T_2 S_1^\infty$	in $S_1^\infty$
$\nu$	0	real	$2K$	$2K + p.\text{imag.}$	$2K + iK'$ $\frac{\sqrt{1+\lambda} - \sqrt{1-\lambda}}{\lambda\sqrt{2}}$	$2K + p.\text{imag.}$	$2K + 2iK'$	$2iK' + \text{real.}$	$4K + 2iK'$	$4K + p.\text{imag.}$	$4K + iK'$ $\frac{\sqrt{1+\lambda} + \sqrt{1-\lambda}}{\lambda\sqrt{2}}$	$4K + p.\text{imag.}$	$4K$
$\xi$	$\infty$	pos. imag.	0	pos. real	$\frac{\sqrt{1+\lambda} - \sqrt{1-\lambda}}{\lambda\sqrt{2}}$	pos. real	0	pos. imag.	$\infty$	pos. real	$\frac{\sqrt{1+\lambda} - \sqrt{1-\lambda}}{\lambda\sqrt{2}}$	pos. real	$\infty$
$\dot{\xi}$	$\infty$	neg. imag.	$-\frac{i}{2}$	neg. imag.	0	pos. imag.	$+\frac{i}{2}$	pos. imag.	$\infty$	neg. imag.	0	pos. imag.	$\infty$
$I$	$\infty$	pos. real	$\infty$	pos. imag.	0	neg. imag.	$\infty$	neg. real	$\infty$	pos. imag.	0	neg. imag.	$\infty$

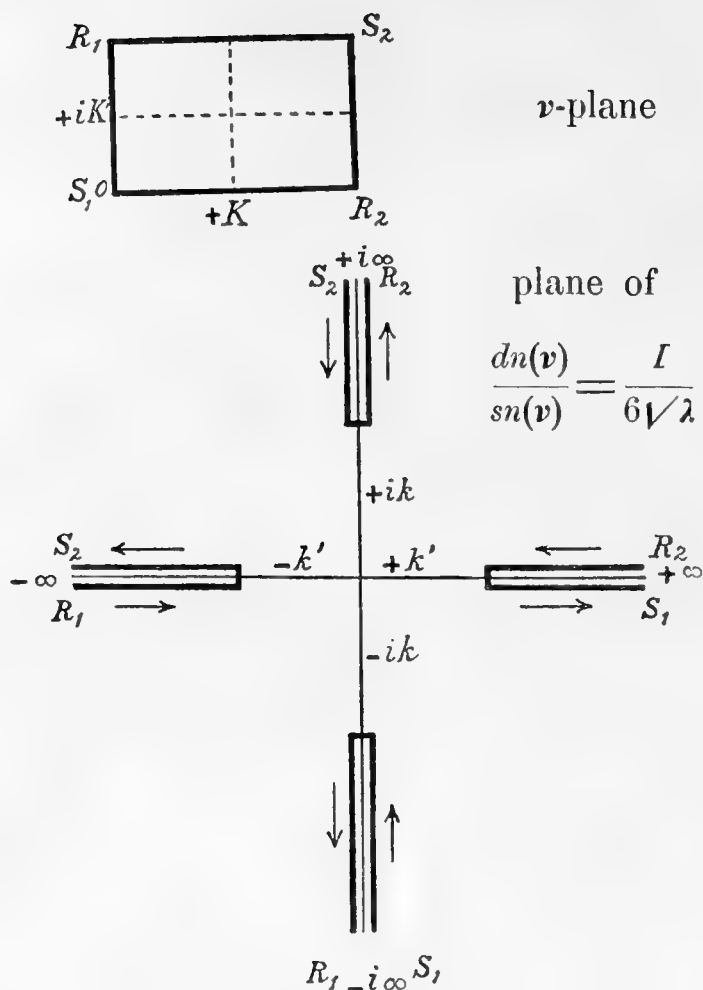


Fig. 1

$I_4 = 6 \sqrt{\frac{1-\lambda}{2}} = 6i \sqrt{\frac{\lambda-1}{2}}$ ; the quotient  $\frac{dn(v)}{sn(v)}$  assumes in those points successively the values  $0, \infty, \pm k', \pm ik$ . The corresponding values of  $v$  are congruent (*mod.*  $2K$  and  $2iK'$ ) with  $K + iK', 0, K$  and  $iK'$ . (see fig. 1).

*Case IVa.* Point  $O$  lies in the domain between the hyperbola and the asymptotes. The points  $R_1, R_2, S_1, S_2, T_1$  and  $T_2$  are all real;  $T_1$  and  $T_2$  lie both on the same side of the polar line of  $O$  as  $O$  itself. We shall assume that the polar line intersects that branch on which  $T_1$  lies. The order of the singular points is then  $S_1, R_1, T_1, R_2, S_2, T_2, S_1$ .

The values  $I_1 = 0, I_2 = \infty, I_3 = 6 \sqrt{\frac{1+\lambda}{2}}, I_4 = 6 \sqrt{\frac{1-\lambda}{2}}$  correspond resp. to the values of  $0, \infty, \pm 1$  and  $\pm k$  for  $\frac{1}{sn(v)}$ , thus to the values of  $v$  which are congruent (*mod.*  $2K$  and  $2iK'$ ) resp. with  $iK', 0, K$  and  $K + iK'$ . (see fig. 2).

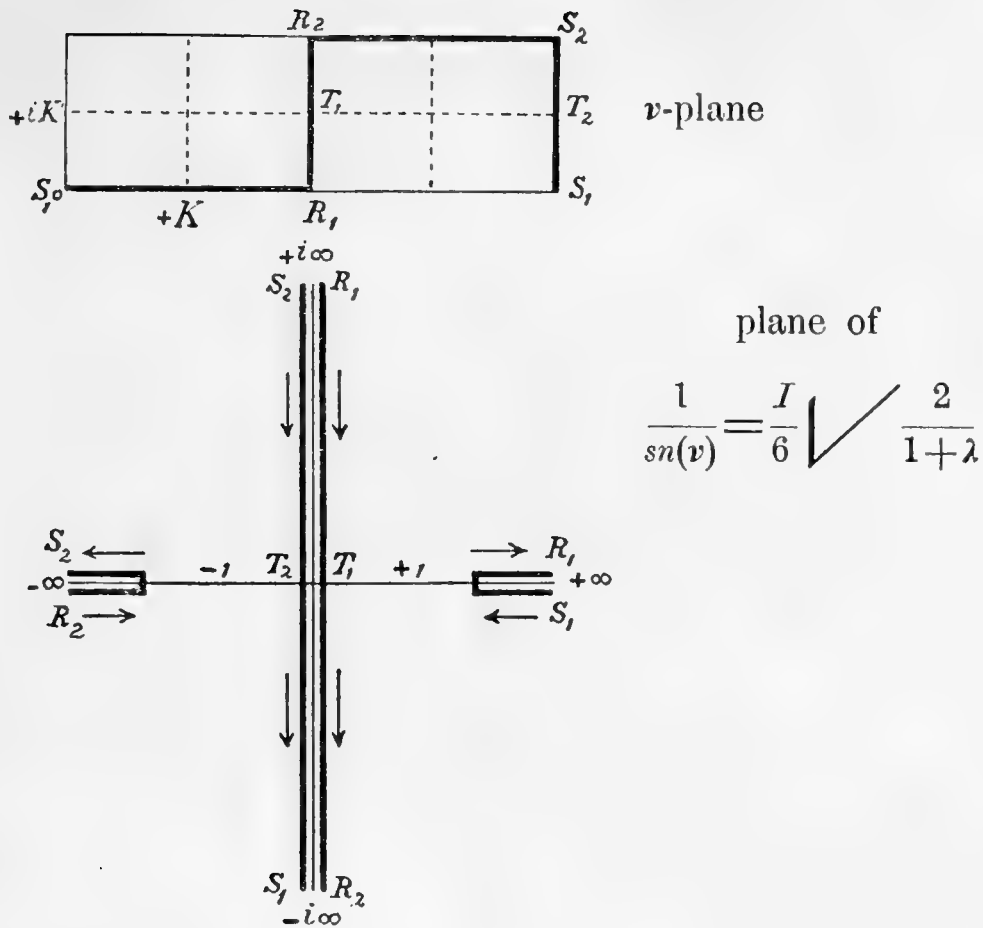


Fig. 2.

Case IVb. Point  $O$  lies inside the ellipse;  $T_1$  and  $T_2$  are real,  $R_1, R_2, S_1$  and  $S_2$  are imaginary.

IVb	in $T_1$	on $T_1T_2$	in $T_2$	on $T_2T_1$	in $T_1$
$v$	$iK'$	$iK' + \text{real}$	$2K + iK'$	$iK' + \text{real}$	$4K + iK'$
$\xi$	$\frac{\sqrt{1+\lambda} + \sqrt{1-\lambda}}{\lambda\sqrt{2}}$	pos. real	$\frac{\sqrt{1+\lambda} - \sqrt{1-\lambda}}{\lambda\sqrt{2}}$	pos. real	$\frac{\sqrt{1+\lambda} + \sqrt{1-\lambda}}{\lambda\sqrt{2}}$
$\zeta$	0	neg. real	0	pos. real	0
$I$	0	pos. real	0	neg. real	0

The points where the motion of  $I$  changes its sign are according to what was found in IVa the points for which  $\frac{1}{sn(v)} = \pm k$ , thus  $v = K + iK'$  (mod.  $2K$  and  $2iK'$ ) (see fig. 3).

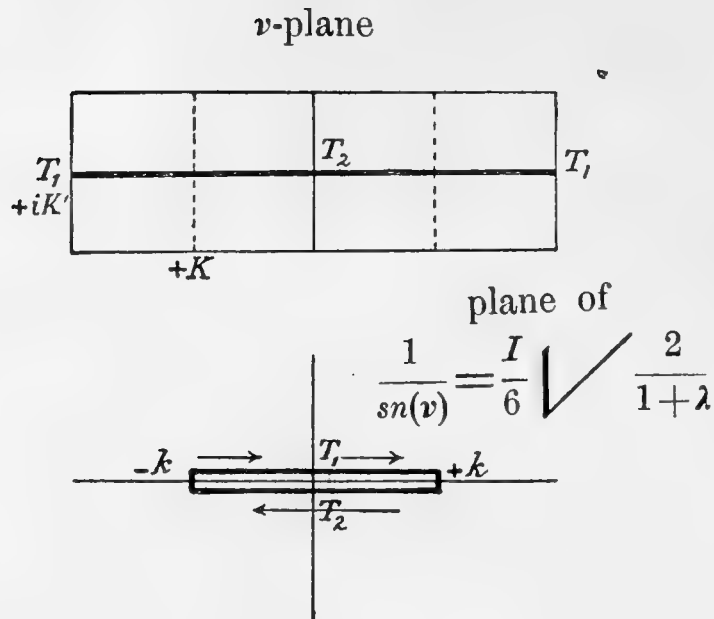


Fig. 3.

*Case VIa.* Point  $O$  lies on the concave side of the hyperbola:  $S_1, S_2, T_1$  and  $T_2$  are real,  $R_1$  and  $R_2$  are imaginary. Let  $T_1$  be the point of intersection of the diameter through  $O$  lying on the same side of the polar line as  $O$  itself.

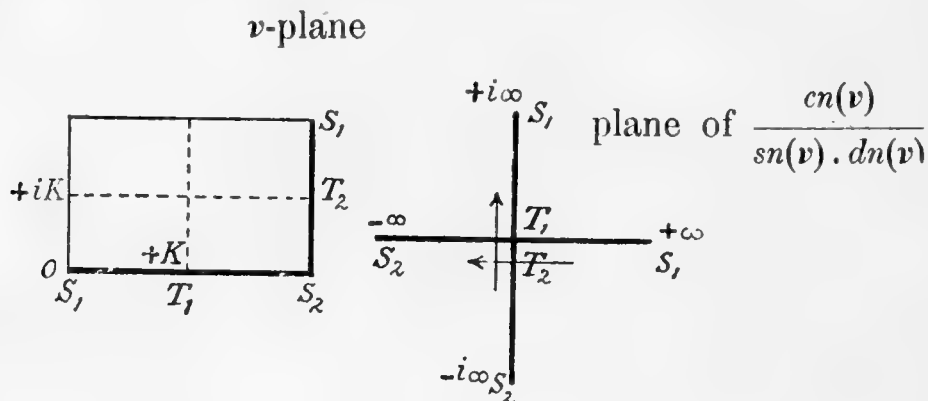


Fig. 4.

The values  $I_1=0$ ,  $I_2=\infty$ ,  $I_3=6 \sqrt{\frac{1+i\lambda'}{2}}$ ,  $I_4=6 \sqrt{\frac{1-i\lambda'}{2}}$  correspond here respectively to the values  $0$ ,  $\infty$ ,  $\pm \sqrt[4]{\frac{1+i\lambda'}{1-i\lambda'}}$  and  $\pm \sqrt[4]{\frac{1-i\lambda'}{1+i\lambda'}}$  for  $\frac{cn(v)}{sn(v) \cdot dn(v)}$ , thus to the values of  $v$  which are congruent (*mod.*  $2K$  and  $K+iK'$ ) with  $K, 0, \frac{1}{2}(K+3iK'), \frac{1}{2}(K+iK')$  (see fig. 4).

*Case VIb.* Point  $O$  lies outside the ellipse;  $R_1, R_2, T_1$ , and  $T_2$  are real,  $S_1$  and  $S_2$  are imaginary. The point of intersection  $T_1$  may lie on the same side of the polar line as  $O$  itself.

For the particular values of  $I$  and the corresponding values of  $v$  we can refer to VIa. (see fig. 5).



Vla	in $S_1^\infty$	on $S_1 T_1$	in $T_1$	on $T_1 S_2^\infty$	in $S_2^\infty$	on $S_2^\infty T_2$	in $T_2$	on $T_2 S_1^\infty$	in $S_1^\infty$
1	0	real	$K + \frac{\sqrt{-1 + \sqrt{1 + \lambda'^2}}}{\lambda'}$	real	$2K$	$2K + \text{p. imag.}$	$2K + iK' + \frac{\sqrt{+1 + \sqrt{1 + \lambda'^2}}}{\lambda'}$	$2K + \text{p. imag.}$	$2K + 2iK'$
2	$\infty$	pos. real	0	pos. real	$\infty$	pos. imag.	0	pos. imag.	$\infty$
3	$\infty$	neg. real	0	pos. real	$\infty$	neg. real	0	pos. real	$\infty$
4	$\infty$	pos. real	0	neg. real	$\infty$	neg. imag.	0	pos. imag.	$\infty$

V1b	in $R_1$	on $R_1 T_1$	in $T_1$	on $T_1 R_2$	in $R_2$	on $R_2 T_2$	in $T_2$	on $T_2 R_1$	in $R_1$
1	$K + iK'$	$K + \text{p. imag.}$	$K + 2iK' - \frac{\sqrt{-1 + \sqrt{1 + \lambda'^2}}}{\lambda'}$	$K + \text{p. imag.}$	$K + 3iK'$	$3iK' + \text{real}$	$2K + 3iK' - \frac{\sqrt{+1 + \sqrt{1 + \lambda'^2}}}{\lambda'}$	$3iK' + \text{real}$	$3K + 3iK'$
2	0	neg. real	0	neg. real	0	neg. imag.	0	neg. imag.	0
3	$\frac{i}{2}$	pos. imag.	0	neg. imag.	$-\frac{i}{2}$	neg. imag.	0	pos. imag.	$\frac{i}{2}$
4	$\infty$	pos. imag.	0	neg. imag.	$\infty$	neg. real	0	pos. real.	$\infty$

Before investigating the cases of degeneration III and V we shall occupy ourselves for a moment with the relation (53) (4<sup>th</sup> comm. p. 1011), existing between  $I$  and  $I^2$ . In the case of the conic it takes the shape of (65) (4<sup>th</sup> comm. p. 1018). The curve it represents is as can be expected symmetrical with respect to the  $X$ -axis ( $X = I^2$ ). To simplify the reasoning we shall translate the curve  $\Phi(X, Y) \equiv \Phi(I^2, I) = 0$  parallel to the  $X$ -axis and we shall decrease it and that by the formulae of transformation

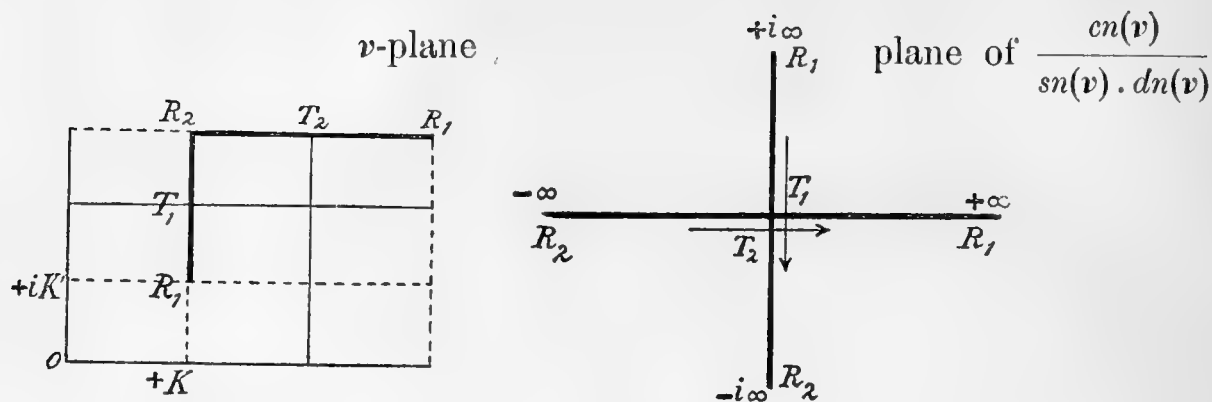


Fig. 5.

$$I^2 - 18 = 36\xi,$$

$$I = 6\eta.$$

The equation of the curve transformed in this manner runs as follows:

$$\Phi(\xi, \eta) \equiv \xi^2 - \eta^2 - \frac{\lambda^2}{4} = 0;$$

the curve is therefore a rectangular hyperbola. In the cases II and IV the  $\xi$ -axis is the real axis, in case VI the  $\eta$ -axis is the real axis. Each point of the conic  $F(x, y) = 0$  corresponds to *one* point of this rectangular hyperbola whilst to *one* point of  $\Phi = 0$  two points of  $F = 0$  are conjugated. The points for which  $I = 0$  have as absciss  $\xi = -\frac{1}{2}$ . The line  $\xi = -\frac{1}{2}$  does not intersect the curve  $\Phi$  in case II, but it does in the cases IV and VI. The point at infinity on  $\xi + \eta = 0$  represents the points  $S_1$  and  $S_2$ ; the point at infinity on  $\xi - \eta = 0$  represents the two points  $R_1$  and  $R_2$ . The points  $T_1$  and  $T_2$  are represented by the points of intersection of  $\Phi = 0$  with  $\xi = -\frac{1}{2}$ . The images of the points  $T_1$  and  $T_2$  are in case VI united in the point of intersection of  $\xi = -\frac{1}{2}$  with the branch of  $\Phi = 0$  lying under the  $\xi$ -axis. The images of  $T_1$  and  $T_2$  are always points where the motion changes its sign along the curve  $\Phi$ .

Now we have to investigate the cases of degeneration.

*Case III<sup>a</sup>.*  $\lambda = +1$ ,  $\sigma_1 = 0$ ,  $a_{13}$  and  $a_{23}$  not disappearing at the same time.

The point  $O$  lies on one of the asymptotes, without coinciding with the centre. So this position occurs with the hyperbola only.

Here equation (71) holds, in which is put  $\tau_0 = 0$ ,

$$I = \pm \frac{6}{\sin \tau} \dots \dots \dots (71')$$

Equation (62) (4<sup>th</sup> comm. p. 1015) passes, on account of the relation

$$a_{33}A_{33} = \Delta,$$

and with the aid of (72), into

$$I^2 = \frac{9}{\zeta^2} (-\zeta^4 + 2\zeta^2 - 1) = -\frac{9(\zeta^2 - 1)^2}{\zeta^2},$$

from which ensues, in connection with (71),

$$\frac{6}{\sin \tau} = \pm \frac{3i(\zeta^2 - 1)}{\zeta},$$

or

$$\zeta = \pm \frac{i(1 \pm \cos \tau)}{\sin \tau}.$$

We choose for  $\zeta$ :

$$\zeta = +i \frac{1 - \cos \tau}{\sin \tau} = +i \operatorname{tg} \frac{\tau}{2}, \quad \dots \dots \dots (85)$$

and find in this manner

$$\zeta = + \frac{i}{2} \sec^2 \frac{\tau}{2}.$$

Now the equations (76) and (77) are incompatible. If they depended on each other we should have  $A_{33} = 0$ , which has not been supposed to be the case.

Equation (77) now runs:

$$a_{13}x + a_{23}y = -a_{33}z \sec^2 \frac{\tau}{2} \quad \dots \dots \dots (86)$$

Bringing this equation into connection with  $F(x, y, z) = 0$ , we find

$$\begin{aligned} 2A_{13} \sec^2 \frac{\tau}{2} \cdot x &= \left\{ a_{22}a_{33} \sec^4 \frac{\tau}{2} - a_{23}^2 \left( 2 \sec^2 \frac{\tau}{2} - 1 \right) \right\} z \\ 2A_{23} \sec^2 \frac{\tau}{2} \cdot y &= \left\{ a_{11}a_{33} \sec^4 \frac{\tau}{2} - a_{13}^2 \left( 2 \sec^2 \frac{\tau}{2} - 1 \right) \right\} z \end{aligned} \quad (87)$$

These formulae can be used unless either  $A_{13}$  or  $A_{23}$  is zero. Therefore we will mention also the expressions for  $x$  and  $y$  for the case  $A_{13} = 0$ . Then we have  $a_{23} = 0$  on account of  $a_{13}A_{13} + a_{23}A_{23} = 0$ . We then find immediately out of (86) the expression for  $x$ , out of the second equation (87) in which  $A_{23}$  is replaced by  $a_{12}a_{13}$  the expression for  $y$ . So the solution is:

$$a_{13}x = -a_{33}z \cdot \sec^2 \frac{\tau}{2}$$

$$2a_{12}a_{13} \sec^2 \frac{\tau}{2} y = \left\{ a_{11}a_{33} \sec^4 \frac{\tau}{2} - a_{13}^2 \left( 2 \sec^2 \frac{\tau}{2} - 1 \right) \right\} z.$$

*Case III<sup>b</sup>.*  $a_{13} = a_{23} = 0$ .

The point  $O$  coincides with the centre.

Now we have

$$I = 0.$$

The expressions for  $x$  and  $y$  are of the form:

$$\begin{aligned} x &= (\alpha e^{i\tau} + \alpha' e^{-i\tau}) z, \\ y &= (\beta e^{i\tau} + \beta' e^{-i\tau}) z. \end{aligned}$$

In order to have  $F \equiv a_{11}x^2 + 2a_{12}xy + a_{22}y^2 + a_{33}z^2 = 0$ , we must put:

$$\begin{aligned} \alpha &= \sigma(-a_{12} + \sqrt{-A_{33}}), & \alpha' &= \sigma'(-a_{12} - \sqrt{-A_{33}}), \\ \beta &= \sigma a_{11}, & \beta' &= \sigma' a_{11} \end{aligned}$$

with the condition

$$\sigma\sigma' = \frac{a_{33}}{-4a_{11}A_{33}}.$$

In the case of the real ellipse we have  $A_{33} > 0$  and  $\frac{a_{33}}{a_{11}} < 0$ . We then can put:

$$\sigma = \sigma' = \frac{1}{2} \sqrt{\frac{-a_{33}}{a_{11}A_{33}}}.$$

So we find

$$\begin{aligned} x &= \frac{1}{2} \sqrt{\frac{-a_{33}}{a_{11}A_{33}}} \cdot \{-a_{12}(e^{i\tau} + e^{-i\tau}) + i\sqrt{A_{33}}(e^{i\tau} - e^{-i\tau})\} z = \\ &= \sqrt{\frac{-a_{33}}{a_{11}A_{33}}} \cdot (-a_{12} \cos \tau - \sqrt{A_{33}} \sin \tau) z, \\ y &= \frac{1}{2} \sqrt{\frac{-a_{33}}{a_{11}A_{33}}} \cdot a_{11}(e^{i\tau} + e^{-i\tau}) z = \sqrt{\frac{-a_{11}a_{33}}{A_{33}}} \cdot \cos \tau \cdot z. \end{aligned} \quad (88)$$

We can use the same expression if we have to deal with a hyperbola not intersecting the  $x$ -axis. For then  $A_{33} < 0$  and  $\frac{a_{33}}{a_{11}} > 0$ , so  $\sigma = \sigma'$  real. We prefer to write  $-\sqrt{-A_{33}} \cdot sh(i\tau)$  for  $\sqrt{A_{33}} \cdot \sin \tau = -i\sqrt{-A_{33}} \cdot \sin \tau$  and  $ch(i\tau) \cos$  for  $\tau$ . Then real points of the hyperbola correspond to purely imaginary values of  $\tau$ .

If the hyperbola does intersect the  $x$ -axis we have  $A_{33} < 0$  and  $\frac{a_{33}}{a_{11}} < 0$ , so  $\sigma = \sigma'$  imaginary.

We then put  $\sigma = -\sigma' = \frac{1}{2} \sqrt{\frac{a_{33}}{a_{11}A_{33}}}$  and get in this manner

$$\begin{aligned} x &= \frac{1}{2} \sqrt{\frac{a_{33}}{a_{11}A_{33}}} \cdot \{-a_{12}(e^{i\tau} - e^{-i\tau}) + \sqrt{-A_{33}}(e^{i\tau} + e^{-i\tau})\} z = \\ &= \sqrt{\frac{a_{33}}{a_{11}A_{33}}} \cdot \{-a_{12} sh(i\tau) + \sqrt{A_{33}} ch(i\tau)\} z, \\ y &= \frac{1}{2} \sqrt{\frac{a_{33}}{a_{11}A_{33}}} \cdot a_{11}(e^{i\tau} - e^{-i\tau}) z = \sqrt{\frac{a_{11}a_{33}}{A_{33}}} \cdot sh(i\tau) \cdot z. \end{aligned} \quad (88)'$$

Here also  $\tau$  must describe in its complex plane the imaginary axis.

For  $a_{11} = 0$ , we get  $(2a_{12}x + a_{22}y)y + a_{33} = 0$ .

A solution of this is given by

$$x = \frac{-1}{2a_{12}} (a_{22}e^{i\tau} + a_{33}e^{-i\tau}),$$

$$y = e^{i\tau}.$$

Here also only purely imaginary values of  $\tau$  come in consideration, as might be expected.

The second case of degeneration (IV) presents itself for  $\lambda = 0$ , i. e.  $\sigma_1 = +1$ . Here we must distinguish three subdivisional cases, viz.

*IV<sup>a</sup>*.  $a_{33} = 0$ : the point  $O$  lies on the conic,

*IV<sup>b</sup>*.  $A_{33} = 0$ : the conic is a parabola,

*IV<sup>c</sup>*.  $a_{33} = 0$  and  $A_{33} = 0$ : the point  $O$  lies on the parabola.

*Case IV<sup>a</sup>*. Here we have (70a) (4<sup>th</sup> comm. p. 1017); substitution of  $\tau_0 = 0$  furnishes

$$I = +3\sqrt{2} \cdot th \frac{\tau}{\sqrt{2}}, \dots \dots \dots (70'a)$$

so

$$i = \frac{3}{ch^2 \frac{\tau}{\sqrt{2}}}$$

Now the equations (62) and (63) (4<sup>th</sup> comm. p. 1015) teach us

$$g = a_{13}x + a_{23}y = \frac{2\Delta \dot{I}z}{3A_{33}} = \frac{2\Delta z}{A_{33}} \cdot \frac{1}{ch^2 \frac{\tau}{\sqrt{2}}}$$

$$A_{23}x - A_{13}y = \sqrt{-A_{33}g^2 + 2\Delta gz} = \sqrt{\left(-\frac{4\Delta^2}{A_{33}^2} \cdot \frac{1}{ch^4 \frac{\tau}{\sqrt{2}}} + \frac{4\Delta^2}{A_{33}^2} \cdot \frac{1}{ch^2 \frac{\tau}{\sqrt{2}}}\right) \cdot z}$$

$$= \frac{2\Delta z}{A_{33}} \cdot \frac{sh \frac{\tau}{\sqrt{2}}}{ch^2 \frac{\tau}{\sqrt{2}}};$$

so we get

$$\left. \begin{aligned} x &= \frac{2z}{A_{33}ch^2 \frac{\tau}{\sqrt{2}}} \left( A_{13} + a_{23} \sqrt{A_{33}} \cdot sh \frac{\tau}{\sqrt{2}} \right) \\ y &= \frac{2z}{A_{33}ch^2 \frac{\tau}{\sqrt{2}}} \left( A_{23} - a_{13} \sqrt{A_{33}} \cdot sh \frac{\tau}{\sqrt{2}} \right) \end{aligned} \right\} \dots \dots (89)$$

In the case  $A_{33} < 0$  we prefer to write  $i\sqrt{-A_{33}} \cdot sh \frac{\tau}{\sqrt{2}} =$   
 $= +\sqrt{-A_{33}} \cdot sin \frac{i\tau}{\sqrt{2}}$  for  $\sqrt{A_{33}} \cdot sh \frac{\tau}{\sqrt{2}}$  and  $cos \frac{i\tau}{\sqrt{2}}$  for  $ch \frac{\tau}{\sqrt{2}}$ .

So, whilst the formulae (89) are specially suitable for the ellipse we do better in using for the hyperbola

$$\left. \begin{aligned} x &= \frac{2z}{A_{33} \cos^2 \frac{i\tau}{\sqrt{2}}} \left( A_{13} + a_{23} \sqrt{-A_{33}} \cdot sin \frac{i\tau}{\sqrt{2}} \right) \\ y &= \frac{2z}{A_{33} \cos^2 \frac{i\tau}{\sqrt{2}}} \left( A_{23} - a_{13} \sqrt{-A_{33}} \cdot sin \frac{i\tau}{\sqrt{2}} \right) \end{aligned} \right\} \dots (89')$$

Consequently the real points of the hyperbola correspond to purely imaginary values of  $\tau$ .

Case IV<sup>b</sup>. Putting  $\tau_0 = 0$ , (70b) (4<sup>th</sup> comm. p. 1017) we find

$$I = -3\sqrt{2} \cdot th \frac{\tau}{\sqrt{2}} \dots (70'b)$$

and therefore

$$I = -\frac{3}{ch^2 \frac{\tau}{\sqrt{2}}}.$$

So the formulae (62) and (63) now give

$$g = a_{13}x + a_{23}y + a_{33}z = -\frac{3a_{33}z}{2I} = \frac{a_{33}z}{2} ch^2 \frac{\tau}{\sqrt{2}},$$

i.e.

$$a_{13}x + a_{23}y = \frac{a_{33}z}{2} \left( ch^2 \frac{\tau}{\sqrt{2}} - 2 \right)$$

and

$$A_{23}x - A_{13}y = \sqrt{2\Delta gz - \Delta a_{33}z^2} = \sqrt{a_{33}\Delta} \cdot z \cdot sh \frac{\tau}{\sqrt{2}},$$

so we find

$$\left. \begin{aligned} x &= \left\{ \frac{a_{23} \sqrt{a_{33}\Delta}}{\Delta} sh \frac{\tau}{\sqrt{2}} + \frac{a_{33}A_{13}}{2\Delta} \left( ch^2 \frac{\tau}{\sqrt{2}} - 2 \right) \right\} z, \\ y &= \left\{ \frac{-a_{13} \sqrt{a_{33}\Delta}}{\Delta} sh \frac{\tau}{\sqrt{2}} + \frac{a_{33}A_{23}}{2\Delta} \left( ch^2 \frac{\tau}{\sqrt{2}} - 2 \right) \right\} z. \end{aligned} \right\} \dots (90)$$

Case IV<sup>c</sup>. Here we have

$$I = \pm 3\sqrt{2}$$



methods which show more satisfactorily the progressive change of the reactions, and thus to find out the real structure of the substance prepared by FAUCONNIER.

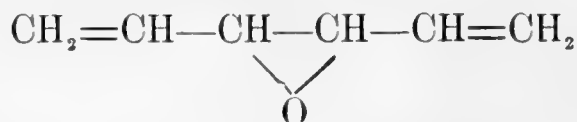
As starting material was used the doubly unsaturated glycol  $\text{CH}_2=\text{CH}-\text{CHOH}-\text{CHOH}-\text{CH}=\text{CH}_2$ , which GRINER prepared by reduction of acrylaldehyde, divinylglycol.

Advantage was taken of the property of acetyl chloride to act on divalent alcohols in such a manner, that of the two alcohol-groups the one is converted into the hydrochloric, the other into the acetic ester.

The reaction product of acetyl chloride on divinylglycol is obtained as a colourless liquid, which after repeated fractionation under a pressure of 18 mM. boils at  $84^\circ-88^\circ$ . I have not yet obtained it in a perfectly pure state as the chlorine content was found a little too high. On keeping, the liquid darkens after a few days and then shows an acid reaction.

In order to prepare the oxide from the chloroacetine it was shaken for some time with strong aqueous sodium hydroxide and then distilled under reduced pressure (to prevent as much as possible, polymerisation). Of the distillate, which consists of two layers, the upper one is again distilled a few times over sodium hydroxide and finally over finely divided calcium in an atmosphere of hydrogen in order to obtain the product completely free from halogen and water.

The so prepared divinylethylene oxide



is a very mobile, colourless liquid, boiling at the ordinary pressure at  $108^\circ-109^\circ$ , with a very pungent odour characteristic of allyl compounds.

$$n_D^{15} = 1,44942. \quad d_{15} = 0,8834.$$

Once obtained in a pure state the oxide is permanent and only turns pale yellow on long keeping; under the influence of alkalis it resinifies when in contact with the air. When brought into contact with hydrogen chloride, this is absorbed immediately; on warming with water, divinylglycol is regenerated.

The ring  $\text{—C—C—}$  is also opened comparatively easily by



amines.

For, if divinylethylene is heated with allylamine for a few hours



a compound is formed of 1 mol. of oxide and 1 mol. allylamine. By distillation and recrystallisation from petroleum ether, I obtained white needles melting at  $37,5^{\circ}$ . The oxide when heated with ammonia also gave a crystallised amino-alcohol.

Another method often applied to arrive at internal ethers consists in addition of hypochlorous acid to an unsaturated hydrocarbon and subsequent elimination of hydrogen chloride from the chlorhydrine formed. Before applying this method to hexatriene which might yield an oxide of the formula  $C_6H_8O$ , I first tried the action of this acid on a hydrocarbon with only one conjugated system of double bonds.

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \text{1.} \quad \text{2.} \quad \text{3.} \quad \text{4.} \end{array}$$

The hydrocarbon isoprene, which is now

readily prepared in a pure condition by means of the so-called HARRIES isoprene lamp, was cooled in ice-water and shaken in the dark with a solution of hypochlorous acid in such proportion that 1 mol. of acid was used for 1 mol. of isoprene.

The hypochlorous acid disappears spontaneously and the isoprene dissolves. After saturation of the liquid with common salt, ether extracts from this solution a compound boiling at  $142^{\circ}-145^{\circ}$ , the chlorine content of which points to its having the composition  $C_5H_9OCl$ . By removing from this compound hydrogen chloride by means of strong aqueous potassium hydroxide, I obtained a liquid with an ethereal odour b.p.  $80^{\circ}-82^{\circ}$  which, however, still contained a trace of halogen.

Brought into contact with hydrogen chloride the latter is at once absorbed; when dissolved in carbon tetrachloride, the substance decolorises, although slowly, a solution of bromine.

If now we consider to which position in the isoprene molecule the HOCl can be attached the three following possibilities may occur.

1. The hypochlorous acid is attached to the double bond 1=2.
2. The hypochlorous acid is attached to the double bond 3=4.
3. or, because the two double bonds are in conjunction, the linking has taken place at the carbon atoms 1 and 4 with the appearance of a new double bond between the carbon atoms 2 and 3. In the latter case a 5-ring would, probably, have been produced from the chlorhydrine thus formed, namely a methyl-dihydrofuran. The ready absorption of hydrogen chloride does not, however, support the latter view.

I hope to be soon able to make further communication on this subject with which I am still occupied.

Utrecht, April 1912.

Org. Chem. Lab. University.

**Chemistry.** — “*The radioactivity of rubidium and potassium compounds.*” II. By Dr. E. H. BÜCHNER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of April 26, 1912).

Some time ago I described a series of experiments undertaken with the object of demonstrating the radioactivity of rubidium and eventually of other alkali metals by the photographic method<sup>1)</sup>. I then only noticed an action on the sensitive plate with rubidium sulphate; the salts of other alkalis produced no effect. I have repeated these experiments and, as announced previously, I have inquired more in particular, whether the phenomenon might be attributable to a previous exposure of the salt to the light; in that case there can be no question of a real radioactivity, but we should have here an analogism of the wellknown experiments with calcium sulphide. According to NIEWENGLOWSKI, this substance acts on a photographic plate by means of rays which penetrate through aluminium, but only when it has been previously exposed to the light. In the present meaning of the word we cannot call calcium sulphide radioactive, because an external influence is at work; if the same happened with rubidium and potassium, these substances could neither be included among the radioactive ones. And because they differ in various respects from the other active substances, there is still some doubt left about this matter. It was, therefore, desirable to carry out some experiments in this direction.

For this purpose I have exposed, simultaneously, in one box, some photographic plates to the action of  $\text{RbCl}$ ,  $\text{RbNO}_3$  and  $\text{Rb}_2\text{SO}_4$  in the manner described previously, but of each salt two specimens were taken; one of these had been kept in complete darkness from 4 to 5 months, the other had been exposed to broad daylight for some days previous to the experiment. When developing after 90 days, no difference was found between the action of the two specimens, both having affected the plates in the same manner. Hence, it again becomes more probable that we are dealing here indeed with true radioactivity.

For the rest I have been able to confirm my previous results. Again, I have not succeeded in getting an action on the sensitive plate either with salts of potassium or with salts of caesium, sodium, and lithium, but on the other hand rubidium did affect the plate. With  $\text{RbCl}$  and  $\text{RbNO}_3$ , also with  $\text{Rb}_2\text{SO}_4$  I found that the plate had

<sup>1)</sup> These Proc. 1909, p. 154.

darkened distinctly on those spots, where little holes or figures had been cut in the screen of copper foil which had been placed between the salt and the plate. The action is strongest with the chloride and weakest with the sulphate. I attribute this to the greater absorption which the rays undergo in the sulphate itself, for this salt has a higher density than the chloride and, therefore may be expected to show a greater absorption. This explanation can also serve for a few deviating results. In two experiments, it appeared that  $\text{Rb}_2\text{SO}_4$  had produced no effect; now in these cases the salt had accidentally been used in the form of fairly large crystals and not in powder, as usual. The surface of the powder is, of course, larger and consequently more rays will reach the plate than in the case where crystals are employed. Perhaps, this reasoning may explain also the results of STRONG<sup>1)</sup> who, in the exposure of different potassium salts to photographic plates, observed effects of very varying intensity; for instance strong action with potassiumcyanide and practically none with the urate.

The rubidium salts investigated by me were obtained from different dealers (MERCK, KAHLBAUM, DE HAEN, SCHUCHARDT); the fact that they show no difference in action goes to prove that the phenomenon must be attributed really to rubidium and not to some impurity.

2. Other investigators have already shown that the radiation of potassium and rubidium consists mainly, probably even exclusively, of  $\beta$ -rays. Now,  $\alpha$ -rays may, however, elude observation sometimes, as they act but faintly on sensitive plates and consequently practically not at all with slightly active substances. Moreover when we are dealing with  $\alpha$ -particles of very small velocity and corresponding small penetrating power, only an exceedingly small portion of the  $\alpha$ -particles will arrive in the surrounding gas and the ionisation current, generated by them, which is measured with the electroscope, will be very weak; it may even be of little importance in regard to the current caused by the  $\beta$ -rays. If now we may apply the results obtained with strongly active substances to feebly active compounds, the  $\alpha$ -rays, if present here, may be expected to possess a slight velocity, since we may assume as a rule: the larger the activity of a substance, the greater the velocity of the  $\alpha$ -particles. A possible occurrence of  $\alpha$ -rays demands an investigation all the more, because the absorption of the radiation in different substances, like tin foil

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<sup>1)</sup> Amer. Chem. Journ. 42, 127.

for instance, cannot be represented by a simple exponential formula; on the contrary, it seems as if the radiation is composed of a part decidedly penetrating and of another one less so; the latter is then only of slight importance.

In two ways, I have attacked the problem of the presence of  $\alpha$ -rays; firstly by observing whether zinc sulphide became luminous under the influence of the salts. This method has the advantage that we can bring together the salt and the zinc sulphide as closely as we like, and reduce as far as possible the absorption which the  $\alpha$ -particles undergo in the air; consequently we may, perhaps, find in this manner  $\alpha$ -rays of very slight penetrating power which would not be detected by other means.

We know that light emitted under the influence of  $\alpha$ -particles possesses a peculiar character and that, when examined under the microscope, it breaks up into numerous points which are formed at the spots, where the  $\alpha$ -particles meet the zinc sulphide; each scintillation, therefore, indicates an  $\alpha$ -particle. In order to show the  $\alpha$ -particles eventually present, an object-slide with a little KCl was put under the microscope; above it at a distance of about 2 m.m. was placed another slide which was coated at its lower surface, by means of Canada balsam, with a layer of zinc sulphide. The whole arrangement is placed in the dark; it is, however, advisable, in imitation of REGENER, to faintly illuminate a portion of the field of vision (for which purpose a "VERKADE waxine" light is very serviceable) in order to facilitate the adjustment. In this manner, we can readily show the  $\alpha$ -particles of pitchblende, uranium oxide, and thorium oxide; we shall be able to observe also all  $\alpha$ -particles which can traverse a distance of at least 2 m.m. in the air. Neither with KCl, nor with RbCl, however, any scintillation was noticed in different experiments, though the observation lasted each time ten minutes. I then made the experiment in another way: to render the distance between the salt and the zinc sulphide as small as possible, I mixed the two compounds. But even then I did not succeed in observing a single flash of light. These experiments thus confirm the results communicated by HENRIOT<sup>1)</sup> in a paper which appeared after my experiments were closed, namely that rubidium and potassium do not emit  $\alpha$ -rays.

3. There is yet another way to demonstrate the emission of  $\alpha$ -particles. It is well known that the heat generated by radium and other radioactive substances originates in the kinetic energy of the  $\alpha$ -particles, which are stopped in the surrounding matter. A large

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<sup>1)</sup> Comptes Rendus, 152, 1384 (1911).

portion of the  $\alpha$ -rays gets already absorbed in the emitting substance, because they penetrate into solid matter but a few hundredths of a m.m.; consequently the active substance is heated above the temperature of the surrounding air and, of course, remains warmer, because the radiation process proceeds continuously.  $\alpha$ -Particles which do not possess a sufficient velocity to ionise gases, or to render the zinc sulphide luminous, may still have a considerable kinetic energy; and when they are absorbed, their energy being converted into heat, they might raise the salt from which they originate to a higher temperature. This argument has also been applied by GREINACHER<sup>1)</sup> during an investigation on the radioactivity of several ordinary substances; he, however, did not study the salts which are now of particular interest to us.

I have investigated this question by placing in a large galvanised iron basin, on pieces of cork, two silvered vacuum flasks of about  $1\frac{1}{2}$  litre capacity. The basin was placed in another and the space between was filled with ice; the whole was placed in a wooden box isolated by means of slag-wool. A third bath serves as a cover, which was also filled with ice and covered with blankets. In this manner, the flasks are entirely surrounded by ice, and it may be assumed that the surrounding air possesses a constant temperature. Every two days, the accumulated water is drawn off and fresh ice is added. The flasks are filled with about 2 kilogrammes of potassium or sodium chloride respectively, and closed with a solid plug of cotton-wool, upon which is poured a layer of paraffin. Through this seal penetrates a very thin-walled glass tube which reaches to the centre of the bulb and contains one of the junctions of a thermo-couple copper-constantan. The constantan wire connects directly the junctions, the copper wires are carried away through an opening in the box and connected to the galvanometer which is suspended according to JULIUS and read off by means of a mirror and a telescope.

If now potassium chloride emits  $\alpha$ -rays, it may be expected to reach a higher temperature than sodium chloride and, owing to a thermoelectric force the galvanometer will deviate; by gauging with a definite difference in temperature it may be found with how many degrees corresponds a deviation of, say, 1 mm.; this proved to be  $0.003^\circ$ . As soon as the circuit is closed a deviation of the galvanometer is observed, but without further discussion we may not conclude to a difference in temperature between the two salts. There are, necessarily, always some places of contact between different

<sup>1)</sup> Ann. der Phys. [4] 24, 79 (1907).

metals which, perhaps, have not exactly the same temperature and therefore also yield a thermo-current. This influence may be eliminated by placing between the galvanometer and the thermoelement a commutator; on commuting, only that part of the current which has to be measured, namely the current of the thermoelement itself, takes another direction; it may, therefore, be determined from the difference. Only care must be taken that no differences in temperature occur in the commutator itself. As such served two three-limbed glass tubes well wrapped up in cotton-wool and placed in a little box, which was suspended and moveable round a horizontal axis. In both tubes was poured a little mercury, while in each of the limbs were introduced wires which effected communication with the galvanometer and the thermoelement, respectively. By inclining the box to  $45^\circ$  in any direction, the current is closed, but this, in both cases, passes through the galvanometer in a different direction. There is still another source of error due to the thermoelement itself whose wires are often not quite homogeneous; and if there should be no equal temperature over their whole length, a thermo-current may be generated. Although these irregularities seem to occur but rarely with copper wires (and only these were here at different temperatures), care was taken all the same that they should not influence the final result, by changing the junctions in the two flasks after a series of measurements.

We then must take again the difference of the resulting figures of different series to obtain the thermo-electric force of the copper-constantan and to calculate thence the difference in temperature between the potassium and sodium chloride. I refrain from giving a detailed communication of the results of the measurements because, anyhow, my conclusion must be that the two salts do not show a difference in temperature, at least none exceeding  $0,001^\circ$ . As I look upon this figure as representing the accuracy attained, I do not attach any importance to the fact that the final result showed sodium chloride to be about  $0.001^\circ$  warmer than potassium chloride. Four experiments were carried out, the junctions of the thermoelement being changed after each; an experiment consisted of five to six measurements which were each composed of three to seven readings, carried out one after another with continuous commutation.

From these experiments also, I must conclude to the absence of  $\alpha$ -rays in potassium compounds; this result did not afford reason to make also an experiment with rubidium chloride.

My best thanks are due to Dr. A. H. W. ATEN, who placed his galvanometer at my disposal for these experiments.

*Inorg. Chem. Laboratory University of Amsterdam.*

**Mathematics.** — “On a differential equation of SCHLÄFLI.” By Prof. J. C. KLUYVER.

As a suitable example of the method of solution due to PFAFF SCHLÄFLI has determined the general integral of the equation

$$a_1 (x_2 p_3 - x_3 p_2)^2 + a_2 (x_3 p_1 - x_1 p_3)^2 + a_3 (x_1 p_2 - x_2 p_1)^2 = 1$$

(Annali di matematica pura ed applicata, serie 2, t. II, p. 89—96) and in his Theorie der partiellen Differentialgleichungen MANSION has repeated the calculation of SCHLÄFLI. As MANSION remarks this treatment of the equation does not allow to maintain the symmetry with respect to the variables; therefore we will show in the following lines that it is possible to obtain the complete integral of the equation with preservation of the symmetry by means of JACOBI'S method.

By putting

$$\begin{aligned} x_2 p_3 - x_3 p_2 &= A_1, \\ x_3 p_1 - x_1 p_3 &= A_2, \\ x_1 p_2 - x_2 p_1 &= A_3 \end{aligned}$$

the given equation passes into

$$f = a_1 A_1^2 + a_2 A_2^2 + a_3 A_3^2 - 1 = 0.$$

The system of simultaneous differential equations to be considered here becomes

$$\frac{dx_1}{a_2 x_3 A_2 - a_3 x_2 A_3} = \dots = \frac{dp_1}{a_2 p_3 A_2 - a_3 p_2 A_3} = \dots$$

One derives from it immediately

$$\frac{dx_1}{a_2 x_3 A_2 - a_3 x_2 A_3} = \frac{dA_1}{(a_2 - a_3) A_2 A_3} = \dots = \frac{\sum A_1 dA_1}{0} = \frac{\sum p_1 dp_1}{0}.$$

This furnishes two integral equations

$$\begin{aligned} f_1 &\equiv p_1^2 + p_2^2 + p_3^2 - m^2 = 0, \\ f_2 &\equiv A_1^2 + A_2^2 + A_3^2 - k^2 = 0. \end{aligned}$$

The two functions  $f_1$  and  $f_2$  are in involution. For we have

$$[A_1^2, p_1^2] = 0, \quad [A_1^2, p_2^2] = 4 A_1 p_2 p_3, \quad [A_1^2 p_3^2] = -4 A_1 p_2 p_3.$$

From this ensues

$$[A_1^2, \sum p_1^2] = 0$$

and furthermore also

$$[f_1, f_2] = 0.$$

So one has to solve the partial derivatives  $p_1, p_2, p_3$  out of the three equations

$$f = 0, \quad f_1 = 0, \quad f_2 = 0$$

and to integrate afterwards the differential equation

$$dz = \sum p_1 dx_1.$$

A direct solution of  $p_1, p_2, p_3$  cannot be given. Therefore we

remark that the three quantities  $A_1, A_2, A_3$  are entirely determined as functions of  $x_1, x_2, x_3$  by the three equations

$$\Sigma A_1^2 = k^2, \quad \Sigma a_1 A_1^2 = 1, \quad \Sigma x_1 A_1 = 0$$

and now we express  $p_1, p_2, p_3$  in  $x_1, x_2, x_3, A_1, A_2, A_3$ .

So by eliminating  $p_2$  and  $p_3$  out of the equations

$$\begin{aligned} x_3 p_1 - x_1 p_3 &= A_2, \\ x_1 p_2 - x_2 p_1 &= A_3, \\ p_1^2 + p_2^2 + p_3^2 &= m^2 \end{aligned}$$

we find that  $p_1$  is determined by the equation

$$p_1^2 \Sigma x_1^2 - 2(A_2 x_3 - A_3 x_2) - x_1^2 m^2 + A_2^2 + A_3^2 = 0,$$

from which follows after some reduction

$$p_1 = \frac{1}{\Sigma x_1^2} \left\{ A_2 x_3 - A_3 x_2 + x_1 \sqrt{m^2 \Sigma x_1^2 - k^2} \right\}.$$

We find for  $p_2$  and  $p_3$  similar expressions; by putting

$$\Sigma x_1^2 = u^2,$$

we get the total differential equation

$$dz = \frac{1}{u^2} \begin{vmatrix} dx_1 & dx_2 & dx_3 \\ A_1 & A_2 & A_3 \\ x_1 & x_2 & x_3 \end{vmatrix} + \frac{du}{u} \sqrt{m^2 u^2 - k^2}.$$

In order to transform the differential

$$dH = \frac{1}{u^2} \begin{vmatrix} dx_1 & dx_2 & dx_3 \\ A_1 & A_2 & A_3 \\ x_1 & x_2 & x_3 \end{vmatrix}$$

we consider three functions  $\xi_1, \xi_2, \xi_3$  of  $A_1, A_2, A_3$ , satisfying the condition

$$\Sigma A_1 \xi_1 = 0,$$

but otherwise arbitrary.

Putting moreover

$$\eta_1 = (A_2 \xi_3 - A_3 \xi_2), \quad \eta_2 = (A_3 \xi_1 - A_1 \xi_3), \quad \eta_3 = (A_1 \xi_2 - A_2 \xi_1),$$

$$\Delta = \begin{vmatrix} \xi_1 & \xi_2 & \xi_3 \\ \eta_1 & \eta_2 & \eta_3 \\ A_1 & A_2 & A_3 \end{vmatrix},$$

we get

$$\Sigma \xi_1 \eta_1 = 0, \quad \Sigma A_1 \eta_1 = 0, \quad \Delta = k^2 \Sigma \xi_1^2 = \Sigma \eta_1^2.$$

We still introduce two quantities  $U$  and  $V$  determined by the equations

$$\Sigma x_1 \xi_1 = U, \quad \Sigma x_1 \eta_1 = V.$$

By adding to these the equation

$$\Sigma x_1 A_1 = 0,$$



and solving  $x_1, x_2, x_3$  out of them we find

$$x_1\Delta = k^2 U\check{\xi}_1 + V\eta_1, \quad x_2\Delta = k^2 U\check{\xi}_2 + V\eta_2, \quad x_3\Delta = k^2 U\check{\xi}_3 + V\eta_3,$$

from which ensues immediately

$$\Sigma x_1^2 = u^2 = \frac{1}{\Delta} (U^2 k^2 + V^2),$$

and also

$$\begin{aligned} \Delta \Sigma x_1 d\check{\xi}_1 &= \frac{1}{2} U d\Delta + V \Sigma \eta_1 d\check{\xi}_1, \\ \Delta \Sigma x_1 d\eta_1 &= -k^2 U \Sigma \eta_1 d\check{\xi}_1 + \frac{1}{2} V d\Delta, \\ \Delta \{V \Sigma x_1 d\check{\xi}_1 - U \Sigma x_1 d\eta_1\} &= (U^2 k^2 + V^2) \Sigma \eta_1 d\check{\xi}_1. \end{aligned}$$

The reduction of the differential  $dH$  now takes place as follows. We have

$$dH = \frac{1}{u^2 \Delta} \begin{vmatrix} dx_1 & dx_2 & dx_3 \\ A_1 & A_2 & A_3 \\ x_1 & x_2 & x_3 \end{vmatrix} \cdot \begin{vmatrix} \check{\xi}_1 & \check{\xi}_2 & \check{\xi}_3 \\ \eta_1 & \eta_2 & \eta_3 \\ A_1 & A_2 & A_3 \end{vmatrix} = \frac{1}{u^2 \Delta} \begin{vmatrix} \Sigma \check{\xi}_1 dx_1 & \Sigma \eta_1 dx_1 & \Sigma A_1 dx_1 \\ 0 & 0 & k^2 \\ U & V & 0 \end{vmatrix}$$

and therefore

$$\begin{aligned} dH &= -\frac{k^2}{u^2 \Delta} \begin{vmatrix} dU - \Sigma x_1 d\check{\xi}_1 & dV - \Sigma x_1 d\eta_1 \\ U & V \end{vmatrix}, \\ dH &= -\frac{k^2 (V dU - U dV)}{U^2 k^2 + V^2} + \frac{k^2}{\Delta} \Sigma \eta_1 d\check{\xi}_1, \end{aligned}$$

so finally

$$dH = k \operatorname{tang}^{-1} \frac{V}{Uk} + \frac{1}{\Sigma \check{\xi}_1^2} \begin{vmatrix} d\check{\xi}_1 & d\check{\xi}_2 & d\check{\xi}_3 \\ A_1 & A_2 & A_3 \\ \check{\xi}_1 & \check{\xi}_2 & \check{\xi}_3 \end{vmatrix}.$$

The second term of the righthand member corresponds in form entirely to the original form  $dH$ ; however the independent variables  $x_1, x_2, x_3$  are replaced now by  $\check{\xi}_1, \check{\xi}_2, \check{\xi}_3$ , functions of  $A_1, A_2, A_3$ .

On account of the equations

$$\Sigma A_1^2 = k^2, \quad \Sigma a_1 A_1^2 = 1,$$

we may consider  $A_1, A_2, A_3$  as functions of one variable  $t$  only, which implies that also  $\check{\xi}_1, \check{\xi}_2, \check{\xi}_3$  appear as functions of that variable  $t$ , whilst this variable itself is determined by the equation

$$\Sigma x_1 A_1 = 0$$

as a function of  $x_1, x_2, x_3$ .

Substituting the expression found for  $dH$  we now find

$$dz = kd \operatorname{tang}^{-1} \frac{V}{Uk} + \frac{1}{\Sigma \check{\xi}_1^2} \begin{vmatrix} d\check{\xi}_1 & d\check{\xi}_2 & d\check{\xi}_3 \\ A_1 & A_2 & A_3 \\ \check{\xi}_1 & \check{\xi}_2 & \check{\xi}_3 \end{vmatrix} + \frac{du}{u} \sqrt{m^2 u^2 - k^2}$$

and

$$z + C = k \operatorname{tang}^{-1} \frac{\sum x_1 (A_2 \xi_3 - A_3 \xi_2)}{k \sum x_1 \xi_1} + \int \frac{1}{\sum \xi_1^2} \begin{vmatrix} \frac{d\xi_1}{dt} & \frac{d\xi_2}{dt} & \frac{d\xi_3}{dt} \\ A_1 & A_2 & A_3 \\ \xi_1 & \xi_2 & \xi_3 \end{vmatrix} dt + \\ + \sqrt{m^2 \sum x_1^2 - k^2} + k \sin^{-1} \frac{k}{m \sqrt{\sum x_1^2}}.$$

So a solution of the given differential equation containing three constants of integration  $C, m, k$  has been obtained; we can now still investigate in what manner this solution can be transformed by means of a suitable choice of the functions  $\xi_1, \xi_2, \xi_3$  into the most simple form.

The only condition  $\xi_1, \xi_2, \xi_3$  have to satisfy is

$$\sum A_1 \xi_1 = 0.$$

So we may put

$$\xi_1 = A_1(a_1 k^2 - 1) \quad , \quad \xi_2 = A_2(a_2 k^2 - 1) \quad , \quad \xi_3 = A_3(a_3 k^2 - 1),$$

or

$$\xi_1 = A_1 b_1 \quad , \quad \xi_2 = A_2 b_2 \quad , \quad \xi_3 = A_3 b_3$$

The equations

$$\sum A_1^2 = k^2 \quad , \quad \sum a_1 A_1^2 = 1$$

can be replaced by

$$\sum A_1^2 = k^2 \quad , \quad \sum b_1 A_1^2 = 0,$$

and these two are satisfied by putting

$$\frac{A_1}{\sqrt{(b_2 - b_3)(t + b_2 b_3)}} = \frac{A_2}{\sqrt{(b_3 - b_1)(t + b_3 b_1)}} = \\ = \frac{A_3}{\sqrt{(b_1 - b_2)(t + b_1 b_2)}} = \frac{k}{\sqrt{-(b_2 - b_3)(b_3 - b_1)(b_1 - b_2)}},$$

where  $t$  is supposed to be determined by the equation

$$\sum x_1 \sqrt{(b_2 - b_3)(t + b_2 b_3)} = 0.$$

By eliminating  $A_1, A_2, A_3, \xi_1, \xi_2, \xi_3$  out of the solution found above we get finally

$$z + C = -k b_1 b_2 b_3 \int \frac{dt}{t \sqrt{-4(t + b_2 b_3)(t + b_3 b_1)(t + b_1 b_2)}} - \\ - k \operatorname{tang}^{-1} \frac{\sum x_1 \sqrt{-(b_2 - b_3)(t + b_3 b_1)(t + b_1 b_2)}}{\sum x_1 b_1 \sqrt{(b_2 - b_3)(t + b_2 b_3)}} + \sqrt{m^2 \sum x_1^2 - k^2} + k \sin^{-1} \frac{k}{m \sqrt{\sum x_1^2}}.$$

By this the differential equation is solved and in this solution the symmetry with respect to the independent variables is preserved.

**Physics.** — “*Series in the spectra of Tin and Antimony*”. By T. VAN LOHUIZEN. (Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of April, 26 1912).

In my Thesis for the Doctorate, which will shortly appear, I have used a spectral formula, which expresses this fundamental thought: “For every series the curve obtained by using the parameters (1, 2, 3, etc.) as abscissae and the reciprocal values of the wave-lengths as ordinates, is exactly the same, only referring to another system of axes”. This curve is the curve of the third degree:

$$y = -\frac{N}{x^3}$$

in which  $y = 10^8 \lambda^{-1}$ ,  $x$  is successively: 1, 2, 3 etc., and  $N$  is the universal constant which occurs in the formulae of RYDBERG, RITZ, and MOGENDORFF—HICKS, the universality of which, somewhat more intelligible after the physical meaning which RITZ<sup>1)</sup> has given to it, can hardly be doubted any more. Transferred to one and the same system of axes the general spectral formula becomes for all series:

$$10^8 \lambda^{-1} = b + (x-a) \tan \gamma - \frac{N \sec \gamma}{[(x-a) \cos \gamma - b \sin \gamma - 10^8 \lambda^{-1} \sin \gamma]^2}$$

in which  $a$  and  $b$  are the ordinates of the origin of the original system of axes, and  $\gamma$  the angle of rotation. As I shall demonstrate more at length in my Thesis, the formula may be reduced to:

$$10^8 \lambda^{-1} = b - \frac{N}{[x + a' + c \lambda^{-1}]^2}$$

for small values of  $\gamma$ .

This approximated form closely resembles RITZ's formula, which may, therefore, be considered as an approximation of the one given by me. Also the formulae of RYDBERG ( $c = 0$ ) and of BALMER for the hydrogen series ( $a' = 0$  and  $c = 0$ ) are implied in it as special cases. Accordingly it is also further closely related to the original formula of RYDBERG. This, too, expresses that the curve is the same for all series, but the important difference is that RYDBERG gives the system of axes only a translation, whereas according to my formula there generally appears a — mostly small — rotation of the curve.

The thought of one curve for all series has been embodied in a model which I have had constructed for this purpose, and which contains the most important part of the curve:

<sup>1)</sup> Magnetische Atomfelder und Serienspektren. Ann. d. Phys. 25 p. 660 et seq. 1908.

$$y = - \frac{109675.0}{x^2}$$

and also the axes of the system to which it refers. By a fine division with vernier it is possible to determine the first four figures of the oscillation frequencies expressed in five figures ( $10^8 \lambda^{-1}$ ,  $\lambda$  expressed in ÅU).

It deserves notice that also RYDBERG has designed his curve by means of one model. He says<sup>1)</sup>: "Toutes les courbes ont été tirées à l'aide du même calibre".

This model has proved to be a great help in detecting new series for elements for which no series had been observed up to now. For this investigation I have first chosen the spectra of those elements for which KAYSER and RUNGE<sup>2)</sup> had found "eine andere Art der Gesetzmässigkeit". KAYSER points out already there that when we pass from one MENDELEJEFF group to the next, the series move to the region of the small wave-lengths. He says<sup>3)</sup>: "Es ist also recht gut möglich, dass für weitere Elemente, die Serien im unzugänglichen Gebiet der Schumannschen Strahlen liegen".

From what I have found, the results of which for *Tin* and *Antimony* I communicate here (I hope to publish the results for the other three elements Pb, As, and Bi later) I think I may infer that in general this conclusion is correct, but *that the beginning of a great number of series is found in the already investigated region.*

Whereas for the other elements the finding of series was facilitated, because the parts where the lines converge, had been observed, while later the first terms were added by the discoveries of PASCHEN and others in the ultra red, exactly the opposite takes place for the elements considered here. The initial terms have been observed, and they lie together of all kinds of series; the part where the series begin to converge clearly lies outside the region of observation. So the difficulty was to accomplish the discovery of the series from the few terms that have only been observed of most of these series. Only very few observations on the ZEEMAN-effect for Tin and Antimony have been made, so that at present they do not yet afford sufficient data for the finding of series. It would be desirable that investigations for these elements on the magnetical splitting up of the spectral lines lying more in the ultra violet were carried out. They might throw more light on the series found by me. So as these data were

1) Kon. Svensk Vetensk. Akad. Hand. Vol. 23 p. 152. 1890.

2) Ueber die Spektren der Elemente VII. Abh. Berl. Akad. 1894. Cf. also KAYSER. Handbuch der Spektroskopie. Vol. II, p. 573 et seq.

3) l. c. p. 573.

not at my disposal, I have tried to find the series by means of my model, somewhat led by the estimations of the intensity given by EXNER and HASCHEK<sup>1)</sup>. As these authors give widely divergent and contradictory differences from those of KAYSER and RUNGE<sup>2)</sup>, I have thought that I ought to prefer the former, because they extend over the whole of the spectrum observed by them.

The obtained results follow.

I must not omit mentioning that besides the said estimations of the intensity, also the constant frequency differences found by KAYSER and RUNGE<sup>3)</sup> have furnished a first basis for my investigation.

In the spectrum of *Tin* I have found a series which is represented by the formula :

$$10^8 \lambda^{-1} = 45307.40 - \frac{109675.0}{(x + 1,651360 - 657,42 \lambda^{-1})^2}$$

$x = 1.2 \dots$

the results of which are :

<i>x</i>	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of errors	Intensity
1	3655.92 <sup>4)</sup>	3655.92	0	0.03	5
2	2785.14	2785.14	0	0.03	3
3	2524.05	2524.05	0	0.05	1
4	2408.27	2408.71	-0.44	0.03	1

No more terms have been observed of this series, which need not astonish us, if we consider that in their tables EXNER and HASCHEK indicate by **1** the lines of the least intensity, and that therefore the following lines have probably been too faint. Now this four-term series would have little conclusive force, if it was not in connection with other series, which I have called *Translation series* in my Thesis for the doctorate, because they are obtained by a pure *y*-translation of the curve, and so only differ in their asymptotes. Such translation series are easily shown, as I have proved there, in the spectra in which series are known. By a translation 5187.03 (one of the two differences of frequency discovered by KAYSER and

<sup>1)</sup> Die Spektren der Elemente bei normalem Druck, II, p. 232 and 235.

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

<sup>3)</sup> l. c.

<sup>4)</sup> EXNER and HASCHEK. l. c.

RUNGE), we get a series with the formula :

$$10^8 \lambda^{-1} = 50494,43 - \frac{109675.0}{(x + 1.651360 - 657.42 \lambda^{-1})^2}$$

$x = 1. 2. \dots$

So the series differs from the others only in its asymptote. We find the following lines :

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of errors	Intensity
1	—	3073.15	—	—	—
2	2433.58 <sup>1)</sup>	2433.57	+0.01	0.03	1
3	2231.80	2231.80	0	0.10	—
4	2141.1	2141.19	-0.09	0.20	—
5	2091.7	2092.30	-0.60	0.50	—
6	2063.8	2063.79	+0.01	0.50	—

$\lambda$  3073.15 for  $x = 1$  does not occur in the arc-spectrum of tin. The spark-spectrum has the line  $\lambda$  3071.9, which is given as diffuse and broad. There appears to be good agreement for this series. The terms for  $x = 7.8$  etc. are outside the region of observation.

The translation 5618.84 gives the series with the formula :

$$10^8 \lambda^{-1} = 50926.14 - \frac{109675.0}{(x + 1,651360 - 657,42 \lambda^{-1})^2}$$

$x = 1. 2 . . . .$

which yields :

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of errors	Intensity
1	3032.90 <sup>1)</sup>	3032.90	0	0.03	8
2	2408.27	2408.27	0	0.03	1
3	2209.78	2210.55	-0.77	0.10	—
4	2121.5	2121.57	-0.07	0.20	—
5	2073.0	2073.50	-0.50	0.50	—

For  $\lambda = 2209.78$  LIVEING and DEWAR found  $\lambda = 2210.7$ , which gives a difference of + 0.15. with the value found by me. There is

<sup>1)</sup> EXNER and HASCHER l. c.

further again good agreement here,  $x = 6$  falls just outside the region of observation.

The translation 6923.26 (the other difference of frequency found by KAYSER and RUNGE), yields:

$$10^8 \lambda^{-1} = 52330.66 - \frac{109675.0}{(x + 1,651360 - 657.42 \lambda^{-1})^2}$$

$$x = 1.2 \quad . \quad . \quad .$$

IV

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of errors	Intensity
1	—	2917.48	—	—	—
2	2334.89	2334.93	-0.04	0.03	1
3	2148.7	2148.59	+0.11	0.20	—
4	2063.8	2064.12	-0.32	0.50	—

$x = 5$  is outside the region of observation.  $\lambda$  2917.48 has not been observed.

The translation 8199.87 yields the formula:

$$10^8 \lambda^{-1} = 53507.27 - \frac{109675.0}{(x + 1.651360 - 657.42 \lambda^{-1})^2}$$

$$x = 1.2 \quad . \quad . \quad .$$

V

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of errors	Intensity
1	2812.72 <sup>1)</sup>	2812.72	0	0.05	3
2	2267.30	2267.33	-0.03	0.05	1
3	2091.7	2091.23	+0.47	0.50	—

$x = 4$  is outside the region of observation.

The translation 8617.50 yields a series with the formula:

$$10^8 \lambda^{-1} = 53924.00 - \frac{109675.0}{(x + 1,651860 - 657,43\lambda^{-k})^2}$$

$$x = 1.2 \quad . \quad . \quad .$$

VI

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of errors	Intensity
1	2779.92	2780.06	-0.14	0.03	4
2	2246.15	2246.06	+0.09	0.10	—
3	2073.0	2073.12	-0.12	0.50	—

$x = 4$  is outside the region of observation.

<sup>1)</sup> EXNER and HASCHKE l.c.

Besides these six series, which are connected by a simple translation, I have found some more in the tin spectrum that are connected. The first series of this group may be represented by the formula:

$$10^8 \lambda^{-1} = 43825.00 - \frac{109675.0}{(x + 1.384406 + 446.70 \lambda^{-1})^2}$$

$$x = 1.2 \dots$$

VII

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of errors	Intensity
1	3801.16	3801.16	0	0.05	30
2	2850.72	2850.72	0	0.03	10
3	2594.49	2594.49	0	0.03	3
4	2483.50	2482.53	+0.97	0.03	3
5	2421.78	2422.24	-0.46	0.03	5
6	2386.96	2385.98	+0.98	0.50	—

Why EXNER and HASCHEK give so great an intensity for  $\lambda$  2421.78, whereas this line is fainter than any of the others according to KAYSER and RUNGE, I do not know.  $\lambda$  2386.96 only occurs with KAYSER and RUNGE with the indication "sehr unscharf". EXNER and HASCHEK have not got this line at all, which is very strange, indeed, in connection with the intensity 5, which KAYSER and RUNGE give.

Of this series I have found two translation series, which correspond with the two differences of frequency found by KAYSER and RUNGE.

The translation 5187.03 yields the series:

$$10^8 \lambda^{-1} = 49012.03 - \frac{109675.0}{(x + 1.384406 + 446.70 \lambda^{-1})^2}$$

$$x = 1.2 \dots$$

VIII

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of Errors	Intensity
1	3175.12	3175.13	-0.01	0.03	100
2	2483.50	2483.49	+0.01	0.03	3
3	2286.75 <sup>1)</sup>	2286.75	0.00	0.03	1
4	2199.46	2199.32	+0.14	0.10	—
5	2151.2	2151.54	-0.34	0.20	—

<sup>1)</sup> EXNER and HASCHEK l.c.



The translation 6923.26 yields the formula :

$$10^8 \lambda^{-1} = 50748.26 - \frac{109675.0}{x + 1.384406 + 446.70 \lambda^{-1})^2}$$

$$x = 1.2 \dots$$

IX

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of Errors	Intensity
1	3009.24	3009.24	0.00	0.05	50
2	2380.82	2380.83	-0.01	0.05	1
3	2199.46	2199.42	+0.04	0.10	—

$\lambda$  2118.43, which we found for  $x = 4$  and the following lines have not been observed. Possibly their intensity is too slight.

These two groups of translation series are represented on the annexed plate, arranged in succession according to the vibration frequencies of the first lines of these series. The figures mean: freq.  $\times 10^3$ . The arrow indicates the limit of the region of observation.

The first line in the fourth red series for Tin must be dotted. The six series that were treated first, have been indicated by the same colour (viz. red), in the same way the three last by black. The succession is: VII, I, VIII, II, III, IX, IV, V, VI.

Not until further investigations on the ZEMMAN-effect have been carried out, will it be possible to determine further what place these series occupy in the whole system. In the arc-spectrum of Tin there are further indications for series, which have, however, not yet been examined by me.

In the spectrum of *Antimony* I have found a series which has as formula :

$$10^8 \lambda^{-1} = 45365.69 - \frac{109675.0}{(x + 1.568667 + 237.63 \lambda^{-1})^2}$$

$$x = 1.2 \dots$$

X

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of Errors	Intensity
1	3383.24	3383.24	0.00	0.03	8
2	2692.35	2692.35	0.00	0.03	3
3	2480.50	2480.50	0.00	0.03	2
4	2383.73 <sup>1)</sup>	2383.93	-0.20	0.03	2+
5	—	2330.95	—	—	—

<sup>1)</sup> EXNER and HASCHEK l.c.

$\lambda$  2330.95 has not been observed, its intensity is possibly too slight.

It lies in the neighbourhood of  $\lambda$  2329.19 of KAYSER and RUNGE, which, however, does not occur at all with EXNER and HASCHEK.

The two following series are in connection with this by translation. The former of them has as formula:

$$10^8 \lambda^{-1} = 43296.20 - \frac{109675.0}{(x + 1.568667 + 237,63 \lambda^{-1})^2}$$

$$x = 1 \ 2 \ \dots$$

XI

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of Errors	Intensity
1	3637.94	3637.95	-0.01	0.03	20
2	2851.20	2851.21	-0.01	0.03	5
3	2614.74	2614.74	0.00	0.03	1
4	2507.90 <sup>1)</sup>	2507.74	+0.16	—	—

$\lambda$  2507.74 does not occur in the arc-spectrum.

In the spark-spectrum, however, we find  $\lambda = 2507.90$  which corresponds with this. Further terms have not been observed on account of their slight intensity.

The other translation-series has as formula:

$$10^8 \lambda^{-1} = 51908.81 - \frac{109675.0}{(x + 1.568667 + 237,63 \lambda^{-1})^2}$$

$$x = 1.2 \ \dots$$

XII

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of Errors	Intensity
1	2770.04	2770.04	0.00	0.03	10 u
2	2289.09	2289.09	0.00	0.10	—
3	2137.21	2135.97	+1.24	0.20	—
4	o. r. o.	2062.26	—	—	—

o. r. o. means outside the region of observation.

Further there are some more indications for other translation series, which lie further in the region of SCHUMANN, viz. that with the asymptotes:

53251.07 to which  $\lambda$  2673.73 (Int. 5) and  $\lambda$  2220.85 belong, and 54951.35 to which  $\lambda$  2554.72. (Int. 1) with  $\lambda$  2139.89 may be counted. For  $x_1 = 3$   $\lambda$  2003.88 is therefore o. r. o.

<sup>1)</sup> EXNER and HASCHEK l.c. Vol. III.

In the Antimony spectrum I found further a second group of translation series, the former of which has as formula:

$$10^8 \lambda^{-1} = 47810.99 - \frac{109675.0}{(x + 1.616567 - 332.37 \lambda^{-1})^2}$$

$$x = 1.2 \dots$$

XIII

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of Errors	Intensity
1	3267.60	3267.60	0.00	0.03	30 u
2	2574.14	2574.14	0.00	0.03	2
3	2360.60	2360.60	0.00	0.03	1+
4	2262.55	2264.49	-1.94	0.20	—
5	2212.54	2212.51	+0.03	0.10	—

Remarkable is the very great deviation for  $x = 4$ , while  $x = 5$  is again in perfect harmony. Earlier investigators HARTLEY and ADENEY found  $\lambda$  2263.5 for this line, which lies just between the value found by KAYSER and RUNGE and mine.

By translation we may obtain the series:

$$10^8 \lambda^{-1} = 45741.50 - \frac{109675.0}{(x + 1.616567 - 332.37 \lambda^{-1})^2}$$

$$x = 1.2 \dots$$

XIV

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of Errors	Intensity
1	3504.64 <sup>1)</sup>	3504.64	0.00	—	3
2	2719.00	2719.00	0.00	0.03	3
3	2481.81	2481.81	0.00	0.03	1
4	o.r.o.	2375.74	—	—	—

$\lambda$  2375.74 lies near  $\lambda$  2373.78, which has been observed, and for which EXNER and HASCHEK remark: 2 +, so diffuse. Possibly this diffuseness is caused by the faint line 2375.74 in the immediate neighbourhood.

Of a number of translation series, which lie for the greater part in the SCHUMANN region, indications are available, which I will give together in the following table with their respective asymptotes, and for each of them one calculated value in the as yet uninvestigated region.

<sup>1)</sup> EXNER and HASCHEK l. c. p. 322.

XV —

XIX Asymptote	53986.13	54354.11	54905.34	55696.37	57039.02
$x = 1$	2719.00	2692.35	2652.70	2598.16	2510.60
$x = 2$	2220.85	2203.13	2175.99	2139.89	2079.55
$x = 3$	2060.25	2044.78	2021.96	1990.20	1938.83

The values for  $x = 3$  lie all in the not investigated region.

Further I have found a third group of translation series in the spectrum of Antimony, the first member of which has as formula:

$$10^8 \lambda^{-1} = 44790.00 - \frac{109675.0}{(x + 1.269826 + 1757.48 \lambda^{-1})^2}$$

$$x = 1.2 \dots$$

XX

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of Errors	Intensity
1	3232.61	3232.61	0.00	0.03	30
2	2652.70	2652.70	0.00	0.03	4
3	2478.40 <sup>1)</sup>	2477.45	+0.95	?	2
4	2395.31	2395.31	0.00	0.03	1
5	n.o.	2349.50	—	—	—

$\lambda$  2349.50 has not been observed any more, which tallies with the course of the intensity, as 1 indicates the faintest lines according to EXNER and HASCHER.

The following form was found as corresponding translation series:

$$10^8 \lambda^{-1} = 52099.97 - \frac{109675.0}{(x + 1.269826 + 1757.48 \lambda^{-1})^2}$$

$$x = 1.2 \dots$$

XXI

$x$	$\lambda_w$	$\lambda_b$	$\lambda_w - \lambda_b$	Limit of Errors	Intensity
1	2614.74	2614.74	0.00	0.03	1
2	2222.10	2221.88	+0.22	0.10	—
3	2098.47	2097.76	+0.71	0.30	—
4	o.r.o.	2038.40	—	—	—

<sup>1)</sup> EXNER and HASCHER loc. cit. p. 232.

while there have been found two indications of series of translation in the region of SCHUMANN viz.

XXII and XXIII	Asymptote =	53402.61	54744.87
$x = 1$		2528.60 (Int. 20)	2445.59 (Int. 2)
$x = 2$		2159.32	2098.47
$x = 3$		2042.40 (o.r.o.)	1987.30 (o.r.o.)

The found series in the Antimony is indicated on the annexed plate, coloured in groups, just as that of the Tin.

The first group of translation series is coloured black, the second group red, the last mentioned group blue. The succession of the black one is: XI, X, XII; that of the red one XIV, XIII, XV, XVI etc.; that of the blue one XX, XXI, XXII and XXIII.

So it appears from this investigation that in the spectra of Tin and Antimony the series have been considerably shifted towards the side of the small wave-lengths, and so that they lie for the greater part in the SCHUMANN region. At the same time it has appeared from it that the intensity of the lines of one and the same series greatly decreases, so that only a limited number of lines has been observed. But though the number of lines is limited, yet the mutual relation that exists between the different members of one translation group, sufficiently proves the existence of series in the same form <sup>1)</sup> as we meet with them for other elements. Though the series there are at once far more pronounced, yet the translation series exists there too, as I shall show more at length in my thesis for the doctorate.

How we must distinguish the series found as principal and subordinate series etc. cannot be decided for the present. Not until a sufficient number of magnetic splittings up have become known in the ultra-violet spectrum of these metals, this investigation can be undertaken. The few things that are known about the ZEEMAN-effect of Sn and Sb, have been found by PURVIS <sup>2)</sup>. We will summarize it here.

PURVIS has measured the magnetic splitting up of the following lines in our tables.

<sup>1)</sup> RYDBERG's statement, therefore (Rapports Paris 1900. T. II. p. 220) that Sn, Sb and some other elements present spectra built according to other laws, cannot be maintained.

<sup>2)</sup> PURVIS Untersuchungen über die ZEEMAN-Phänomene. Physikal. Zeitschr. p. 594. 1907. and the literature mentioned there.

$\lambda$	$\frac{d\lambda}{\lambda^2}$
<i>Tin</i>	
3032.90	+ 2.12 <i>s</i> 0 <i>p</i> - 2.16 <i>s</i>
3801.16	+ 1.22 <i>s</i> 0 <i>p</i> - 1.22 <i>s</i>
2850.72	+ 1.30 <i>s</i> 0 <i>p</i> - 1.30 <i>s</i>
3175.12	+ 2.12 <i>s</i> 0 <i>p</i> - 2.13 <i>s</i>
3009.24	+ 2.00 <i>s</i> 0 <i>p</i> - 2.02 <i>s</i>
<i>Antimony</i>	
3637.94	+ 2.11 <i>s</i> + 0.99 <i>p</i> 0 - 0.99 <i>p</i> - 2.11 <i>s</i>
3232.61	+ 1.76 <i>s</i> 0 <i>p</i> - 1.75 <i>s</i>
2770.04	+ 1.20 <i>s</i> 0 <i>p</i> - 1.20 <i>s</i>
3267.60	+ 1.17 <i>s</i> 0 <i>p</i> - 1.19 <i>s</i>
2598.16	+ 1.60 <i>s</i> 0 <i>p</i> - 1.60 <i>s</i>
2528.60	+ 1.59 <i>s</i> 0 <i>p</i> - 1.59 <i>s</i>

In this table *s* denotes vibrations normal to the field, *p* vibrations parallel to the field. Of the lines of the Table only Sn 3801 and Sn 2851 belong to the same series. They are both blurred, in connection with this the agreement in magnetic splitting up is sufficient.

Sb 3638 becomes a quadruplet. According to PURVIS it is identical with that of Cu 3274 and Ag 3383 and so of Na 5896. It will have to appear from the further investigation of the magnetic field whether this numerical result has a deeper meaning.

In conclusion I will point out some objections, which might be

raised when the above series are studied. In some cases we find, namely, a value given under  $\lambda_w$  which occurs in two series. The corresponding values of  $\lambda_b$  are then somewhat different as a rule. It is now the question :

“Do the observed lines belong to two series, or have we to do with two lines close together, one of which is difficult to distinguish from the other?”

Before answering this question I will first draw attention to this that this phenomenon is also met with in the spectra of other elements. Thus we find in the spectrum of aluminium <sup>1)</sup>  $\lambda$  2204,73 classed as  $n=8$  in the 1st subordinate series, and as  $n=7$  in the 2nd subordinate series; in that of Zinc <sup>2)</sup>  $\lambda$  2430,74 as  $n=8$  in the 2nd component of the 1st subordinate series, and as  $n=9$  in the 1st component of the same series. In the spectrum of Calcium <sup>3)</sup> we find  $\lambda$  3101,87 as  $n=8$  in the 3rd component of the 2nd subordinate series, and as  $n=9$  in the 1st subordinate series. These few examples may suffice to show that the phenomenon that presents itself a few times in the series found by me, is met with elsewhere.

Let us now try to answer the question raised led by the examples which present themselves in our case.

Let us begin with the spectrum of Tin.

For  $\lambda_w$  2483.50 we find  $\lambda_b = 2412.53$  in VII and  $\lambda_b = 2482.49$  in VIII<sub>2</sub>. Examining the observation of this line we find given by KAYSER and RUNGE <sup>4)</sup>: “2 umgekehrt”, and by EXNER and HASCHEK <sup>5)</sup>: “3 unscharf, umgekehrt”. It is not impossible that here two different lines must be observed. Also what follows pleads in favour of this: In VII we find successively the intensities: 30, 10, 3, 3. That for  $x=4$  the intensity is not found smaller than 3 may find its explanation in this, that two lines of slighter intensity give this increased intensity.

For  $\lambda_w$  2408,27, which is given in I<sub>4</sub> with  $\lambda_b = 2408,71$ , in III<sub>2</sub> with  $\lambda_b = 2508.27$ , a similar explanation may hold. KAYSER and RUNGE find <sup>4)</sup>: “3 umgekehrt”, EXNER and HASCHEK <sup>5)</sup>: “1 unscharf.” The course of intensity in I is: 5. 3. 1. 1. Probably  $\lambda_b = 2408.71$  agrees therefore with a very faint line beside  $\lambda$  2408,27, which belongs to III.

$\lambda_w$  2199.46, which has been given in VIII<sub>4</sub> with  $\lambda_b = 2199.32$ , and in IX<sub>3</sub> with  $\lambda_b = 2199.42$ , we find in KAYSER and RUNGE <sup>6)</sup> with the indication: “1 umgekehrt”, and in EXNER and HASCHEK <sup>6)</sup> in the

<sup>1)</sup> KAYSER, Handbuch der Spectroscopie. Vol. II, p. 547.

<sup>2)</sup> l. c. p. 542.

<sup>3)</sup> l. c. p. 536.

<sup>4)</sup> Ueber die Spektren der Elemente. VII. Abh. Berl. Akad. 1894.

<sup>5)</sup> l. c. Vol. II.

<sup>6)</sup> l. c. Vol. III.

sparkspectrum (the arc-spectrum of Tin they have observed no further than  $\lambda$  2267):  $\lambda$  2199.41 "1 unscharf" and  $\lambda$  2199.68 "1 unscharf". So the two lines very clearly appear here very closely side by side.

$\lambda_w$  2091.7 occurs with  $\lambda_b$  2092.30 in  $\text{II}_5$  and with  $\lambda_b$  2091.23 in  $\text{V}_3$ . This line has not been observed by EXNER and HASCHEK.

In KAYSER and RUNGE<sup>1)</sup> we find "3 umgekehrt (?)". So they doubt whether or no they have to do with a reversal here. So the surmise is justified that we have to do here with two separate lines, which surmise is supported if the course of the intensity in II is examined according to the observations of KAYSER and RUNGE. Starting from  $x=2$  this is namely 5, 3, 1, 3, 3. The increased intensity 3 for  $x=5$  is again accounted for by the assumption of two lines close together. In the same way the increased intensity of the line 2063.8, which as  $x=6$  occurs in the same series, may be accounted for by our finding  $\lambda_b=2064,12$  in  $\text{IV}_4$ , which is given there also with  $\lambda_w=2063.8$ . It is a line which has been given by KAYSER and RUNGE<sup>2)</sup> with a limit of errors 0.50, so which could be observed less accurately.

After this extensive discussion of the spectrum of Tin, a few indications will suffice for that of Antimony.

$\lambda$  2719.00 we find in  $\text{XIV}_2$  and  $\text{XV}_1$ . The intensity in XIV is 3.3.1, so somewhat too high for  $x=2$ . This line is found in KAYSER and RUNGE reversed, but not in EXNER and HASCHEK<sup>2)</sup>. This is also the case for  $\lambda$  2692.35, which occurs in  $\text{X}_2$  and  $\text{XVI}_1$ , and with  $\lambda$  2652.70 in  $\text{XX}_2$  and  $\text{XVII}_1$ .

$\lambda$  2614.74 we find as  $\text{XI}_3$  and  $\text{XXI}_1$ . It occurs in both observers as a single line. Noteworthy, however, is the difference in intensity. In KAYSER and RUNGE<sup>3)</sup> this line is one of the strongest lines (intensity 5, while 6 is the greatest intensity that occurs), whereas in EXNER and HASCHEK<sup>4)</sup> it is one of the weakest (intensity 1, highest intensity 30).  $\lambda$  2098.47 has not been observed by EXNER and HASCHEK. We find it given in  $\text{XXI}_3$  and  $\text{XXIII}_2$ . In connection with the  $\lambda_b$  which I found for  $\text{XXI}_3$ , namely 2097.76 I still want to remark that this value lies between that found by KAYSER and RUNGE, and that of HARTLEY and ADENEY, who give for it:  $\lambda$  2096.4.

I should further like to make another remark. When the list on

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1) l. c. Vol. III.

2) l. c.

3) l. c.

4) l. c.



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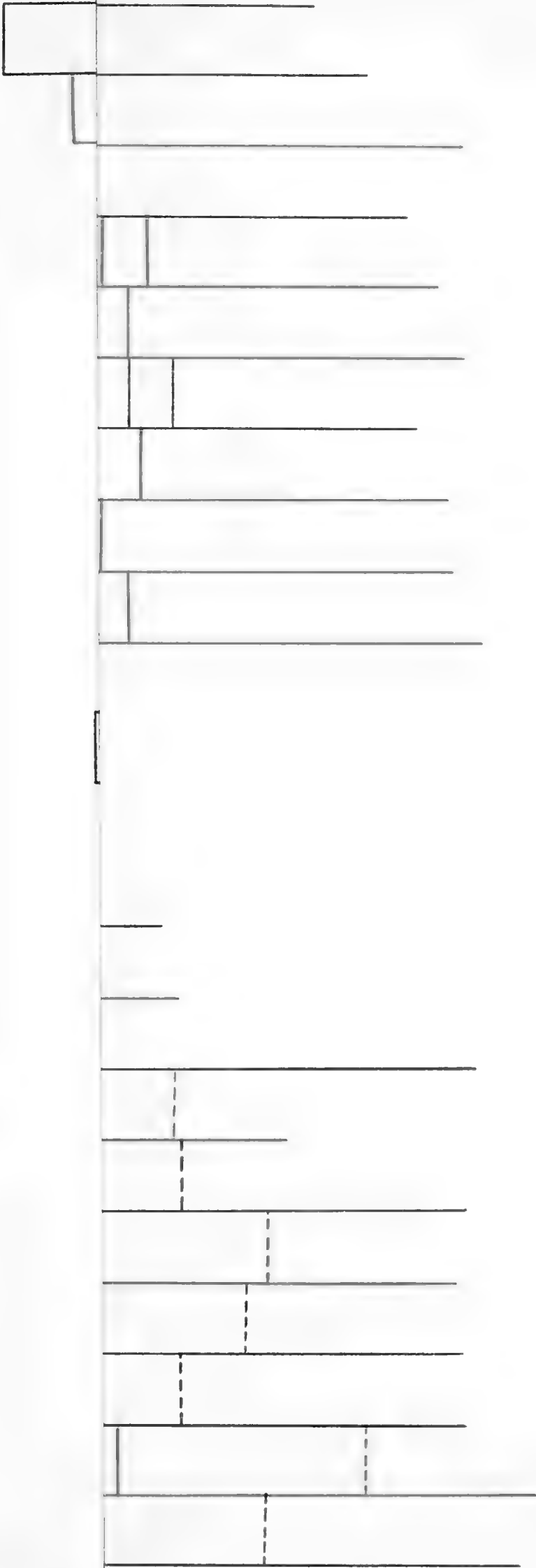
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TIN

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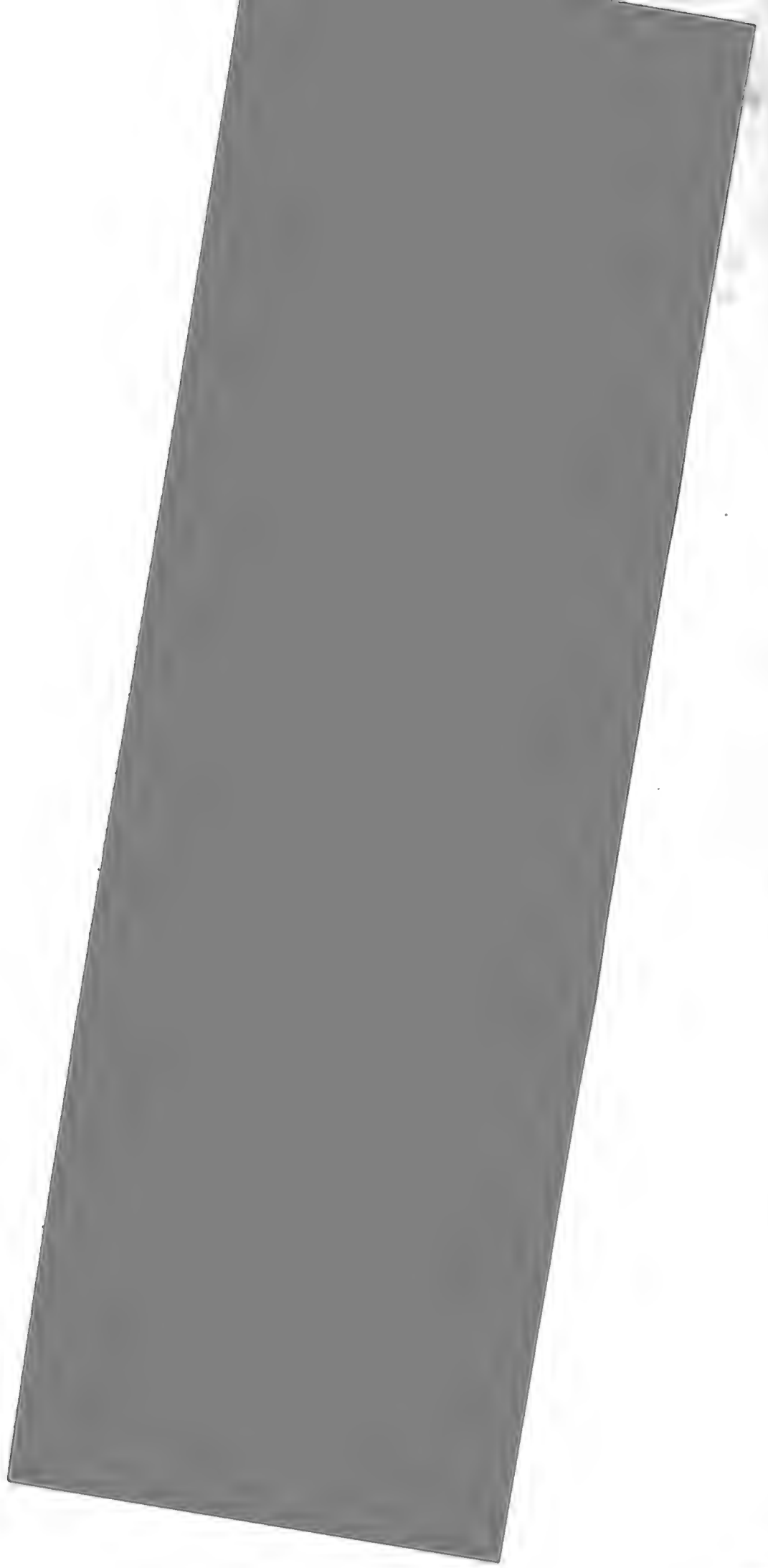
ANTIMONY.

SERIES IN THE SPECTRA  
OF



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p. 42 with the given magnetic separation is examined, the question naturally rises:

“Why do  $\lambda$  3032.90 ( $\text{III}_1$ ) and  $\lambda$  3175.12 ( $\text{VIII}_1$ ) occur in different series for Tin, though they exhibit the same splitting-up?”

The same question applies also for Antimony  $\lambda$  2770.04 ( $\text{XII}_1$ ) and  $\lambda$  3267.60 ( $\text{XIII}_1$ ), and also for Antimony  $\lambda$  2598.16 ( $\text{XVIII}_1$ ) and  $\lambda$  2528.60 ( $\text{XXII}_1$ ).

To answer this question I have traced every time two lines as  $10^8 \lambda^{-1}$  and examined by means of my model without giving it a rotation, what would be about the frequencies of the other terms of the series that is perfectly determined without rotation by these two points. In this way I have arrived at the following results:

If we consider  $\text{Sn } \lambda$  3175.12 as  $x = 3$  and  $\text{Sn } \lambda$  3032.90 as  $x = 4$ , we get  $10^8 \lambda^{-1} = \pm 28400$  for  $x = 1$ , which does not agree with any observed line. (The nearest lines have the frequencies 27353.20 and 30023.63).

If we consider these lines as  $x = 3$  and  $x = 5$ , we find  $10^8 \lambda^{-1} = \pm 32450$  for  $x = 4$ , which does not agree with any line.  $x = 2$  yields  $10^8 \lambda^{-1} = \pm 29500$ , which might then possibly be 30023.63. But this is not very probable either, for the line which

	+ 1.79 s	
	+ 1.22 p	
agrees with this ( $\lambda$ 3330.75) exhibits a quadruplet <sup>1)</sup>	0	in the
	- 1.22 p	
	- 1.79 s	

magnetic field, and so very certainly does not belong to this eventual series. In this way I have ascertained that the lines in question cannot be ranged together with others in one and the same series.

I have obtained corresponding results with the other lines which show the same splitting-up. This has rendered it very probable that the rule: “All the terms of one and the same series present the same resolution in a magnetic field”, cannot be reversed, and so it is my opinion that the argument that I have not ranged lines which present the same splitting up in the same series, cannot be advanced as an objection to the classification of the Tin- and Antimony-spectrum given by me.

<sup>1)</sup> PURVIS. Proc. Cambridge Phil. Soc. 14. 1907, p 220.

**Mathematics.** — “*New researches upon the centra of the integrals which satisfy differential equations of the first order and the first degree.*” (Second Part). By Prof. W. KAPTEYN.

8. Assuming in the third place

$$\begin{aligned} a' + c' &= i(a + c) \\ aa' - cc' &= (b - ib')(a + c) \\ 2b' &= 3a + 5c \end{aligned}$$

or putting  $b = i\beta$

$$\begin{aligned} 2a' &= -i(3a - 2\beta + 3c) \\ 2c' &= i(5a - 2\beta + 5c) \\ 2b' &= 3a + 5c. \end{aligned}$$

We have

$$q_1 = a' - i(3a + 2b') = -\frac{i}{2}(15a - 2\beta + 13c)$$

$$q_2 = 2a + 3b' - ib = \frac{1}{2}(13a + 2\beta + 15c)$$

$$r_0 = -\frac{i}{6}(86a^2 + 26a\beta + 179ac - 4\beta^2 + 28\beta c + 99c^2)$$

$$r_1 = -\frac{1}{4}(45a^2 - 36a\beta + 84ac + 4\beta^2 - 32\beta c + 39c^2)$$

$$r_2 = -\frac{i}{2}(130a^2 - 6a\beta + 265ac - 4\beta^2 - 8\beta c + 137c^2)$$

$$r_3 = \frac{1}{12}(421a^2 + 116a\beta + 972ac - 12\beta^2 + 120\beta c + 567c^2)$$

and for the coefficients of  $P_4$

$$\begin{aligned} s_1 &= (5a + 2b')r_0 + a'r_1 \\ 2s_2 - 4s_0 &= (8b + 2c')r_0 + (4a + 4b')r_1 + 2a'r_2 \\ 3s_3 - 3s_1 &= 3cr_0 + (6b + 3c')r_1 + (3a + 6b')r_2 + 3a'r_3 \\ 4s_4 - 2s_2 &= 2cr_1 + (4b + 4c')r_2 + (2a + 8b')r_3 \\ -s_3 &= cr_2 + (2b + 5c')r_3. \end{aligned}$$

To determine the next condition we introduce the two following polynomia

$$P_5 = t_0x^5 + t_1x^4y + t_2x^3y^2 + t_3x^2y^3 + t_4xy^4 + t_5y^5$$

$$P_6 = u_0x^6 + u_1x^5y + u_2x^4y^2 + u_3x^3y^3 + u_4x^2y^4 + u_5xy^5 + u_6y^6.$$

The coefficients of the first are determined by the relations

$$\begin{aligned}
t_1 &= (6a+2b')s_0 + a's_1 \\
2t_2 - 5t_0 &= (10b+2c')s_0 + (5a+4b')s_1 + 2a's_2 \\
3t_3 - 4t_1 &= 4c's_0 + (8b+3c')s_1 + (4a+6b')s_2 + 3a's_3 \\
4t_4 - 3t_2 &= 3c's_1 + (6b+4c')s_2 + (3a+8b')s_3 + 4a's_4 \\
5t_5 - 2t_3 &= 2c's_2 + (4b+5c')s_3 + (2a+10b')s_4 \\
- t_4 &= cs_3 + (2b+6c')s_4
\end{aligned}$$

which may always be satisfied, and the coefficients of the second are related to those of the first by the following system

$$\begin{aligned}
u_1 &= (7a+2b')t_0 + a't_1 \\
2u_2 - 6u_0 &= (12b+2c')t_0 + (6a+4b')t_1 + 2a't_2 \\
3u_3 - 5u_1 &= 5c't_0 + (10b+3c')t_1 + (5a+6b')t_2 + 3a't_3 \\
4u_4 - 4u_2 &= 4c't_1 + (8b+4c')t_2 + (4a+8b')t_3 + 4a't_4 \\
5u_5 - 3u_3 &= 3c't_2 + (6b+5c')t_3 + (3a+10b')t_4 + 5a't_5 \\
6u_6 - 2u_4 &= 2c't_3 + (4b+6c')t_4 + (2a+12b')t_5 \\
- u_5 &= ct_4 + (2b+7c')t_5.
\end{aligned}$$

This system is impossible unless

$$5u_1 + (3u_3 - 5u_1) + (5u_5 - 3u_3) + 5(-u_5) = 0$$

or

$$\begin{aligned}
(35a+10b'+5c)t_0 + (5a'+10b+3c')t_1 + (5a+6b'+3c)t_1 + \\
+ (3a'+6b+5c')t_3 + (3a+10b'+5c)t_4 + (5a'+10b+35c')t_5 = 0
\end{aligned}$$

which may be written

$$A t_1 + B (2t_2 - 5t_0) + C (3t_3 - 4t_1) + D (4t_4 - 3t_2) + E (5t_5 - 2t_3) + F (-t_4) = 0$$

if

$$\begin{aligned}
A &= \frac{5}{3} (7a' + 14b + 17c') \quad , \quad B = - (7a + 2b' + c), \\
C &= \frac{1}{3} (5a' + 10b + 19c') \quad , \quad D = - \frac{1}{3} (19a + 10b' + 5c), \\
E &= a' + 2b + 7c' \quad , \quad F = - \frac{5}{3} (17a + 14b' + 7c).
\end{aligned}$$

Thus, choosing as before  $s_0 = 0$ , the sought condition takes this form

$$\begin{aligned}
& s_1 [ a'A + (5a + 4b')B + (8b + 3c')C + 3cD ] \\
& + s_2 [ 2a'B + (4a + 6b')C + (6b + 4c')D + 2cE ] \\
& + s_3 [ 3a'C + (3a + 8b')D + (4b + 5c')E + cF ] \\
& + s_4 [ 4a'D + (2a + 10b')E + (2b + 6c')F ] = 0.
\end{aligned}$$

Writing this equation

$$f_1 s_1 + f_2 s_2 + f_3 s_3 + f_4 s_4 = 0$$

and eliminating  $a' b' c'$  we obtain

$$A = \frac{20i}{3} (8a + \beta + 8c) \quad , \quad B = -2(5a + 3c) \quad , \quad C = \frac{4i}{3} (10a - \beta + 10c)$$

$$D = -\frac{2}{3} (17a+15c) \quad , \quad E = 4i(4a-\beta+4c), \quad F = -\frac{10}{3} (19a+21c)$$

$$\begin{aligned} f_1 &= -10(a+c)(13a+10\beta+11c) = 10(a+c)g_1 \\ f_2 &= 30i(a+c)(3a-2\beta+5c) = 10(a+c)g_2 \\ f_3 &= -10(a+c)(31a-2\beta+41c) = 10(a+c)g_3 \\ f_4 &= -10i(a+c)(61a-14\beta+59c) = 10(a+c)g_4. \end{aligned}$$

Now, omitting the factor  $10(a+c)$ , we get

$$g_1 s_1 + g_2 s_2 + g_3 s_3 + g_4 s_4 = 0$$

wherein the values  $s$  may be expressed in function of  $r$  in this way

$$2s_1 = (16a+10c)r_0 - i(3a-2\beta+3c)r_1$$

$$2s_2 = i(5a+6\beta+5c)r_0 + 10(a+c)r_1 - i(3a-2\beta+3c)r_2$$

$$2s_3 = -2cr_2 - i(25a-6\beta+25c)r_3$$

$$2s_4 = \frac{i}{2}(5a+6\beta+5c)r_0 + (5a+6c)r_1 + \frac{i}{2}(7a+2\beta+7c)r_2 + (7a+10c)r_3.$$

Substituting these values, and putting

$$G_1 = 13a + 10\beta + 11c \quad , \quad G_2 = 9a - 6\beta + 15c,$$

$$G_3 = 31a - 2\beta + 41c \quad , \quad G_4 = 61a - 14\beta + 59c$$

we find

$$\begin{aligned} & r_0 [-(16a+10c)G_1 - (5a+6\beta+5c)G_2 + \frac{1}{2}(5a+6\beta+5c)G_4] \\ & + ir_1 [(3a-2\beta+3c)G_1 + 10(a+c)G_2 - (5a+6c)G_4] \\ & + r_2 [(3a-2\beta+3c)G_2 + 2cG_3 + \frac{1}{2}(7a+2\beta+7c)G_4] \\ & + ir_3 [(25a-6\beta+25c)G_3 - (7a+10c)G_4] = 0 \end{aligned}$$

which may be reduced to

$$\begin{aligned} & \frac{1}{2} r_0 [-201a^2 - 72a\beta - 252ac - 12\beta^2 - 36\beta c - 75c^2] \\ & + ir_1 [-176a^2 + 14a\beta - 349ac - 20\beta^2 + 32\beta c - 171c^2] \\ & + \frac{1}{2} r_2 [481a^2 - 48a\beta + 1108ac - 4\beta^2 - 84\beta c + 667c^2] \\ & + ir_3 [348a^2 - 138a\beta + 777ac + 12\beta^2 - 156\beta c + 435c^2] = 0 \end{aligned}$$

Writing this result

$$\frac{1}{3} r_0 T_0 + ir_1 T_1 + \frac{1}{2} r_2 T_2 + ir_3 T_3 = 0$$

and assuming

$$r_0 = -\frac{i}{6} R_0, \quad r_1 = -\frac{1}{4} R_1, \quad r_2 = -\frac{i}{2} R_2, \quad r_3 = \frac{1}{12} R_3$$

we obtain

$$R_0 T_0 + 3R_1 T_1 + 3R_2 T_2 - R_3 T_3 = 0$$

which after reduction gives finally the condition

$$12(a+c)(a-2\beta-c)(3a-2\beta+5c) = 0.$$

This condition breaks up into three others from which the first  $a+c=0$  has already been examined in Art. 2.

9. Introducing the second, we must examine the case where

$$2a' = -i(3a-2\beta+3c)$$

$$2c' = i(5a-2\beta+5c)$$

$$2b' = 3a+5c$$

$$2\beta = a-c$$

or, remembering that  $b=i\beta$

$$a' = -i(a+2c)$$

$$c' = i(2a+3c)$$

$$2b' = 3a+5c$$

$$2b = i(a-c).$$

This case has already been met with in Art. 7.

10. Finally we have the relations

$$2a' = -i(3a-2\beta+3c)$$

$$2c' = i(5a-2\beta+5c)$$

$$2b' = 3a+5c$$

$$2\beta = 3a+5c$$

which are identical with

$$a' = ic$$

$$c' = ia$$

$$2b = 2ib' = i(3a+5c).$$

The differential equation reduces in this case to

$$\frac{dy}{dx} = \frac{-x+icx^2+(3a+5c)xy+ia y^2}{y+ax^2+i(3a+5c)xy+cy^2}$$

whose general integral may be constructed from the two particular integrals

$$(a+3c)(x-iy)^2+2i(x+iy)+\frac{1}{a+c}=0$$

and

$$(a+3c)(x-iy)^2+3i(x^2+y^2)=0$$

which are easily found.

This general integral

$$\frac{\{(a+3c)(x-iy)^2+3i(x^2+y^2)\}^2}{\left\{(a+3c)(x-iy)^2+2i(x+iy)+\frac{1}{a+c}\right\}^3} = \text{const.}$$

may be expanded for small values of  $x$  and  $y$  in the form

$$x^2 + y^2 + F_3 + F_4 + \dots = \text{const.}$$

which proves again that the origin is a centrum.

11. Resuming we may conclude that where

$$(a + c)^2 + (a' + c')^2 = 0.$$

the differential equation

$$\frac{dy}{dx} = \frac{-x + a'x^2 + 2b'xy + c'y^2}{y + ax^2 + 2bxy + cy^2}$$

has a centrum in the origin of coordinates only in the following cases

$$I. a + c = 0 \quad \text{en} \quad a' + c' = 0$$

$$II. a' + c' = \pm i(a + c) \quad \text{en} \quad a + b' = 0$$

$$III. 2a' = \pm i(a - 2b' + c), \quad 2c' = \pm i(a + 2b' + c), \quad 2b = \pm i(a - c)$$

$$IV. a' = \pm ic, \quad c' = \pm ia, \quad 2b' = 3a + 5c, \quad 2b = 3a + 5c$$

for it is easily seen that in the last three cases everywhere  $i$  may be replaced by  $-i$ .

The results obtained in our former paper show that the origin is also a centrum in the three following cases

$$V. a' + c' = 0, \quad a' = b \quad \text{en} \quad a + b' = 0$$

$$VI. a' + c' = 0, \quad a' = b = 0$$

$$VII. a' + c' = 0, \quad a' = b, \quad 2b' = 3a + 5c, \quad ac + b^2 + 2c^2 = 0.$$

We found there one case more viz.

$$a' + c' = 0, \quad a' = b \quad \text{and} \quad a + c = 0$$

but this is included in I.

12. To compare these results with those of DULAC, we will transform our differential equation

$$\frac{dy}{dx} = \frac{-x + a'x^2 + 2b'xy + c'y^2}{y + ax^2 + 2bxy + cy^2} = \frac{-x + Y}{y + X}$$

in his form. This may be done by the substitution

$$h\xi = x + iy \quad k\eta = x - iy.$$

This gives

$$\frac{hd\xi}{y + X + i(-x + Y)} = \frac{kd\eta}{y + X - i(-x + Y)}$$

where

$$y - ix = -ih\xi, \quad y + ix = ik\eta$$

$$X + iY = -i(A - B)h^2\xi^2 - 2i(C - C')hk\xi\eta - i(D - E)k^2\eta^2$$

$$X - iY = -i(D + E)h^2\xi^2 - 2i(C + C')hk\xi\eta - i(A + B)k^2\eta^2$$

and



$$A = \frac{i}{4}(a+2b'-c), \quad B = \frac{1}{4}(a'-2b-c'), \quad C = \frac{i}{4}(a+c)$$

$$D = \frac{i}{4}(a-2b'-c), \quad E = \frac{1}{4}(a'+2b-c'), \quad C' = \frac{1}{4}(a'+c').$$

Thus we find generally

$$\left[ \xi + h(A-B)\xi^2 + 2k(C-C')\xi\eta + \frac{k^2}{h}(D-E)\eta^2 \right] d\eta$$

$$+ \left[ \eta - k(A+B)\eta^2 - 2h(C+C')\xi\eta - \frac{h^2}{k}(D+E)\xi^2 \right] d\xi = 0 \quad (A)$$

and when  $C' = 0$  or  $a' + c' = 0$

$$\left[ \xi + h(A-B)\xi^2 + 2kC\xi\eta + \frac{k^2}{h}(D-E)\eta^2 \right] d\eta$$

$$+ \left[ \eta - k(A+B)\eta^2 - 2hC\xi\eta - \frac{h^2}{k}(D+E)\xi^2 \right] d\xi = 0 \quad (B)$$

where

$$A = \frac{i}{4}(a+2b'-c), \quad B = \frac{2(a'-b)}{4}, \quad C = \frac{i(a+c)}{4}$$

$$D = \frac{i}{4}(a-2b'-c), \quad E = \frac{2(a'+b)}{4}.$$

If now we compare with (B) the first equation (1) of Art. 1 we have

$$h(A-B) = 1, \quad 2kC = \mu, \quad \frac{k^2}{h}(D-E) = \nu$$

$$-k(A+B) = 1, \quad -2hC = \mu, \quad -\frac{h^2}{k}(D+E) = \nu$$

which may be satisfied by taking  $k = -h$  and

$$B = 0, \quad E = 0$$

or

$$a' = b = 0.$$

This first equation therefore belongs to our class VI.

In the same way we may infer that

- (2) belongs to class V
- (3) is a special case of class I
- (4) belongs to class VII
- (7) is a special case of class I
- (9) is a special case of class VI
- (11) is a special case of class I.

If now  $C' \neq 0$  we compare with (A). This gives for the fifth equation of Art 1

$$\begin{aligned}
 h(A-B) &= 1, & 2k(C-C') &= 0, & \frac{k^2}{h}(D-E) &= 0 \\
 -k(A+B) &= 0, & -2h(C+C') &= v, & -\frac{h^2}{k}(D+E) &= v
 \end{aligned}$$

which may be satisfied by

$$A + B = 0, \quad D - E = 0, \quad C - C' = 0$$

or

$$2a' = i(a - 2b' + c), \quad 2c' = i(a + 2b' + c), \quad 2b = i(a - c).$$

Thus (5) belongs to class III.

In the same way it is seen that

(6) is a special case of class II

(8) belongs to class IV

(10) is a special case of class III.

The eleven equations given by DULAC are therefore contained in the preceding 7 classes.

**Chemistry.** — “*On a few oxyhaloids.*” By Prof. F. A. H. SCHREINEMAKERS and Mr. J. MILIKAN.

Of the chlorides, bromides, and iodides of the alkaline earths several oxy-salts have already been described; in order to further investigate the occurrence or non-occurrence of these salts, to determine the limits of concentration between which they exist and, if possible, to find other oxyhaloids, different isotherms have now been determined and by means of the “residue method”<sup>1)</sup> the compositions of the solid phases have been deduced therefrom. Here, we will discuss only the solid substances that can be in equilibrium with solution.

*The system  $\text{CaCl}_2\text{—CaO—H}_2\text{O}$ .*

*Temperature  $10^\circ$  and  $25^\circ$ .* At both these temperatures occur, besides  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$ , as solid phases, the oxychlorides:



the composition of the second salt may be expressed also as:



This latter oxychloride has already been found previously by a determination of the isotherm of  $25^\circ$ <sup>2)</sup>; the first one was then

<sup>1)</sup> F. A. H. SCHREINEMAKERS. Die heterogenen-Gleichgewichte von H. W. BAKHUIS ROOZEBOOM. III<sup>e</sup> 149.

<sup>2)</sup> F. A. H. SCHREINEMAKERS and TH. FIGEË, Chem. Weekbl. 683 (1911).

already known<sup>1)</sup>. From their determinations, SCHREINEMAKERS and FIGEE thought they might conclude that the other oxy-salt should have the composition



As the region of existence of this salt at 25° was, however, still but very small, a slight error in the determination of this composition was still possible.

*Temperature 50°.* At this temperature occur, besides  $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$ , also the two oxychlorides:



as solid substances in proximity to their saturated solutions. The first one already exists at 10° and 25°, the last one had not been described, as yet.

*The system:  $\text{CaBr}_2$ — $\text{CaO}$ — $\text{H}_2\text{O}$ .*

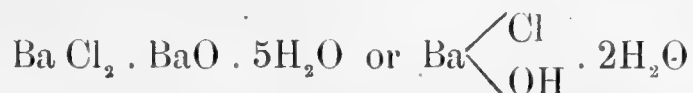
In this system, only the isotherm of 25° has been determined; as solid phases occur, besides  $\text{CaBr}_2 \cdot 6 \text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$ , the oxybromides:



The latter salt was not known up to the present; the first one has been described previously.<sup>2)</sup>

*The system:  $\text{BaCl}_2$ — $\text{BaO}$ — $\text{H}_2\text{O}$ .*

In this system the isotherm of 30° has been determined<sup>3)</sup>; as solid phase occurs here, besides  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$  and  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ , the oxychloride:



This salt had already been prepared and described previously<sup>4)</sup>; the two oxychlorides:



also described previously, were not found at 30°.

*The system:  $\text{BaBr}_2$ — $\text{BaO}$ — $\text{H}_2\text{O}$ .*

In this system the isotherm of 25° has been determined; as solid

1) ROSE, Schweigers Journ. **29**, 155.

DITTE. Compt. rend. **91**, 576.

ANDRÉ, Compt. rend. **92**, 1452.

2) E. TASSILLY. Compt. rend. **119**, 371.

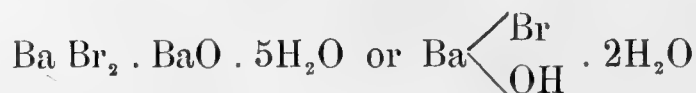
Ann. Chim. et Phys. [7] **17**, 38.

3) F. A. H. SCHREINEMAKERS. Zeitschr. f. Phys. Chem. **68** 88 (1909).

4) BECKMANN, Ber. **14** 2151 (1881)

André. Compt. rend. **93**, 58; **98**, 572.

phase occurs, besides  $\text{Ba Br}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , the oxybromide:



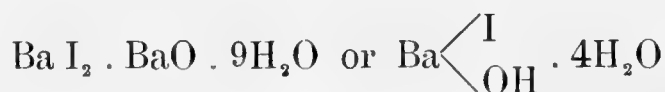
This salt has already been described previously<sup>1)</sup>; the other oxybromide:



which has also been described<sup>4)</sup> was not found at 25°.

*The system: Ba I<sub>2</sub>—BaO—H<sub>2</sub>O.*

In this system also, the isotherm of 25° has been determined; in addition to  $\text{Ba I}_2 \cdot 7\text{H}_2\text{O}$ ,  $\text{Ba I}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  the oxyiodide:



also described previously, occurs as solid phase.<sup>2)</sup>

Besides the above systems, various other ones are now being investigated; the results of this research will be communicated later.

**Physics.** — “*Accidental deviations of density in mixtures*”. By Dr. L. S. ORNSTEIN (Communicated by Prof. H. A. LORENTZ).

The theory of accidental deviations of density in mixtures does not differ, as for the principles, from that of the deviations of density in systems containing only one kind of molecules. To calculate these deviations I shall apply the canonical ensembles of GIBBS<sup>3)</sup>.

1.—Let us suppose a mixture of  $k$  substances to be in a volume  $v$ ,  $n_1$  being the number of molecules of the kind 1,  $n_\alpha$  that of the kind  $\alpha$ , and  $n_k$  that of the kind  $k$ . Besides the coordinates and moments of the centres of gravity, a number of internal coordinates and moments can be used to characterize the state of the molecules. Let us imagine a canonical ensemble built up of those systems. We shall denote by  $x_{11}, y_{11}, z_{11}, \dots, z_{1n_1}$  the coordinates of the centres of gravity for the molecules of the first kind, those of the  $\alpha$ -molecules will be represented by  $x_{\alpha 1} \dots z_{\alpha n_\alpha}$ .

In order further to characterize the system, we shall introduce

1) BECKMANN, J. f. prakt. Chem. N. F., **27** 132 (1883).

2) BECKMANN. Ber. **14**, 2156.  
E. TASSILLY, Compt. rend. **120**, 1338.

3) I shall confine myself to a single phase, the coexistence of phases offering no particular difficulties. I dealt with this question in my dissertation (comp. p. 114).

the moments belonging to the coordinates (the internal ones and those of the centres of gravity) mentioned above. Now, suppose  $d\lambda_i$  to represent an element of the extension in phase of the internal coordinates and moments. Consider the integral

$$\int e^{-\varepsilon'/\Theta} dx_{11} \dots dz_{knk} d\lambda_i,$$

where  $\varepsilon'$  is the total energy  $\varepsilon$  diminished by the energy of the progressive motion of the centres of gravity. The integration with respect to the coordinates of the centres of gravity must be extended over the  $3(n_1 + \dots + n_k)$ -dimensional space  $v^3 \Sigma n_x$ , whereas all values that are possible without dissociation of the molecules are to be ascribed to the internal coordinates and moments.

If, in the case considered, there exists a sphere of repulsion such as there is with rigid, perfectly elastic molecules, then the consequence will be that  $\varepsilon'$  takes an infinite value for certain configurations, and therefore the parts of the integral corresponding with these configurations will not contribute to it. Just as in the case of a simple substance and in that of a binary mixture<sup>1)</sup>, one can show in this case that the integral may be put into the form

$$\left\{ \omega (n_1 \dots n_x \dots n_k) \cdot v^{\sum_{\alpha} n_x} \right\}^1$$

where  $n_x = \frac{n_x}{v}$ , i. e. the number of molecules of the kind  $x$  pro unit of volume.

The function  $\omega$  may be determined if the structure of the molecules is given; but for our purpose it is sufficient for us to know that the integral can be reduced to the form mentioned above.

2. We now imagine the volume  $V$  to be divided into a great number of equal elements of volume  $V_1 \dots V_\lambda \dots V_l$ , and we want to know the number of systems in a canonical ensemble for which the element  $V_\lambda$  contains respectively  $n_{1\lambda} \dots n_{x\lambda} \dots n_{k\lambda}$  of the different molecules. We have for the numbers  $n_{x\lambda}$

$$\sum_1^l n_{x\lambda} = n_x$$

the total number of molecules of each kind being given.

This number of systems  $\zeta$ , which I shall call the frequency of the systems mentioned, is represented by the formula

$$\zeta = N e^{\frac{\Psi}{\Theta}} \prod_1^k \left\{ (2\pi\Theta m_x)^{\frac{3}{2}n_x} n_x! \prod_1^l \left\{ \frac{\omega_\lambda (n_{1\lambda} \dots n_{x\lambda} \dots n_{k\lambda}) V_\lambda^{n_{x\lambda}}}{n_{x\lambda}!} \right\} \right\}, \quad (1)$$

<sup>1)</sup> Comp. my dissertation and these Comm. 1908, p. 107.

$m_z$  denoting the mass of a molecule of the kind  $z$ . We now can ask, for which values of the numbers  $n_{z\lambda}$  this frequency is a maximum. In this way we find for the  $k$  conditions to which the densities in the most frequently occurring system are submitted:

$$-\log n_{z\lambda} + \sum_1^l (n_{z\lambda}) \frac{\delta \log \omega_\lambda}{\partial n_{z\lambda}} + \log \omega_\lambda = f_z, \quad \dots \quad (2)$$

$z$  from 1 to  $k$ . These conditions can be satisfied by means of a homogeneous distribution of each of the  $z$  kinds over the volume  $V$ . Further the second variation of  $\zeta$  or of  $\log \zeta$  has to be negative. If we denote by  $n_{z\lambda}$  the values in the most frequently occurring system, then the frequency  $\xi_\Delta$  of the system in which these numbers have the values  $n_{z\lambda} + \tau_{z\lambda}$  can be represented by

$$\xi_\Delta = \xi_0 e^{-Q} \quad \dots \quad (3)$$

The quantity  $Q$  is a homogeneous quadratic function of the numbers  $\tau_{z\lambda}$ . Taking the sum of  $\xi_\Delta$  with respect to all possible values of these numbers i.e. from  $-\infty$  to  $+\infty$ , we obtain  $\sum \xi_\Delta = N$ , from which  $\Psi$  can be calculated.

Proceeding in this way we find

$$e^{-\frac{\Psi}{\Theta}} = \prod_1^k (2\pi\Theta m_z)^{\frac{3n_z}{2}} \{\omega(n_1 \dots n_z \dots n_k)\}^{n_z}, \quad \dots \quad (4)$$

In calculating  $\Psi$ , which is equivalent to the free energy, we must neglect a factor of the order of unity. However, the formula is rigorously exact, the above-mentioned being a mere verification of the equation (3). For keeping in mind the definition of GIBBS, we have for  $\Psi$

$$e^{-\frac{\Psi}{\Theta}} = \int e^{-\frac{2\varepsilon' + m_z x_{1z}^2}{2\Theta}} m_1 dx_{11} \dots dx_{11} d\lambda_i$$

and therefore

$$e^{-\frac{\Psi}{\Theta}} = \prod_1^k (2\pi\Theta m_z)^{\frac{3}{2}n_z} \int e^{-\frac{\varepsilon'}{\Theta}} dx_{11} \dots dz_{zn_z},$$

and we see that according to the definition of the function  $\omega$ , the formula given for  $\Psi$  holds exactly <sup>1)</sup>.

If we would have as a separate system of volume  $V_\lambda$  the  $n_{1z} \dots n_{z\lambda} \dots n_{z\lambda}$  molecules being now in the volume  $V_\lambda$ , then the free energy of this system would be given by the formula

<sup>1)</sup> Comp. also my dissertation p. 56, 112, 126.

$$e^{-\frac{\Psi_\lambda}{\Theta}} = \prod_1^k (2\pi\Theta m_x)^{\frac{3}{2}n_{x\lambda}} \{\omega(n_{1\lambda} \dots n_{x\lambda} \dots n_{y\lambda}) V_\lambda\}^{n_{x\lambda}}.$$

The function  $\Psi_\lambda$  may be used to transform the formula for the frequency  $\zeta$ . For, applying the theorem of STIRLING, we can write  $\zeta$  in the form

$$\zeta = N e^{\frac{\Psi}{\Theta}} \prod_1^k (2\pi\Theta m_x)^{\frac{3}{2}n_x} \prod_1^l \left\{ \frac{\omega_\lambda(n_{1\lambda} \dots n_{k\lambda}) V_\lambda}{n_{x\lambda}} \right\}^{n_{x\lambda}}$$

and therefore, introducing  $\Psi_\lambda$ , we obtain for  $\zeta$

$$\zeta = N e^{\frac{\Psi}{\Theta}} n_1 \dots n_x \dots n_k \prod_1^l \left\{ e^{-\frac{\Psi_\lambda}{\Theta}} \prod_1^k \frac{1}{n_{x\lambda}} \right\}$$

For the further discussion we shall not use the free energy  $\Psi_\lambda$ , but a function  $\psi_\lambda$ <sup>1)</sup>, closely connected with it, and being defined by the equation

1) We can somewhat more closely explain the introduction of the function  $\psi_\lambda$  (comp. also my dissertation p. 52 s.). We shall compare the free energy of the system considered above to the free energy of the same system in gaseous state and in a volume so great that it can be considered as an ideal gas. We now can easily show the free energy of the mixture in the gaseous state to be equal to the sum of free energies of the components, if each of them occupies the same volume as their mixture. Further we can suppose that the volume of each of the substances (which now occur as simple substances in  $k$  separate volumes), is changed in such a way, that the number of particles pro unit of volume which is to be taken very great, amounts to  $\nu$  (arbitrarily chosen) for all  $k$  systems. The volume occupied by the  $x$ <sup>th</sup> component now amounts to  $\frac{n_{x\lambda}}{\nu}$ . In this state  $\left(\frac{n_{x\lambda}}{\nu}\right)^{n_{x\lambda}}$  will be so great that  $(\omega(\nu)n^{x\lambda})$  may be put equal to unity.

We therefore find for the free energy of each of the components, originating from the element  $\lambda$

$$e^{-\frac{\Psi'_{x\lambda}}{\Theta}} = (2\pi\Theta m_x)^{\frac{3}{2}n_{x\lambda}} \left(\frac{n_{x\lambda}}{\nu}\right)^{n_{x\lambda}}.$$

And for their total free energy :

$$e^{-\frac{\Psi'^\lambda}{\Theta}} = e^{-\frac{\sum_1^k \Psi'_{\lambda x}}{\Theta}} = (2\pi\Theta m_x)^{\frac{3}{2} \sum_1^k n_{x\lambda}} \prod_1^k \left(\frac{n_{x\lambda}}{\nu}\right)^{n_{x\lambda}}$$

For the difference between the free energy in the state from which we started and that in the zero-state considered we find

$$e^{-\frac{\psi_\lambda}{\Theta}} = \prod_1^k \left( \frac{\omega_\lambda V_\lambda}{n_{x\lambda}} \right)^{n_{x\lambda}} = \prod_1^k \left( \frac{\omega_\lambda}{n_{x\lambda}} \right)^{n_{x\lambda}}.$$

Introducing the function  $\psi_\lambda$  we obtain for  $\zeta$

$$\zeta = N e^{\frac{\Psi}{\Theta}} n_1^{n_1} \dots n_x^{n_x} \dots n_k^{n_k} \prod_1^k (2\pi \Theta m_x)^{\frac{3}{2} n_x} \prod_1^l e^{-\frac{\psi_\lambda}{\Theta}}.$$

The volume being given, the function  $\psi$  is a function of the densities  $n_x$ , for

$$-\frac{\psi}{\Theta} = \sum_1^k n_x \{ \log \omega (n_1 \dots n_x \dots n_k) - \log n_x \} = \\ V \sum_1^k \{ n_x \log \omega (n_1 \dots n_x \dots n_k) - \log n_x \}$$

3. We shall use the form now given to  $\zeta$  to put the question of probability of deviations in such a form that the deviations of density appear from our formulae. We then have to examine for which values of the densities  $\log \zeta$  will be a maximum. Suppose  $n_{x\lambda}$  to represent these values and  $\varrho_{x\lambda}$  to represent the deviations of densities for other systems, then

$$\sum_1^l \varrho_{x\lambda} = 0.$$

For  $\delta \log \zeta$  we have

$$\delta \log \zeta = -\frac{1}{\Theta} \left[ \sum_1^l \sum_1^k \frac{\partial \psi_\lambda}{\partial n_{x\lambda}} \varrho_{x\lambda} + \frac{1}{2} \sum_1^l \left\{ \frac{\partial^2 \psi_\lambda}{\partial n_{1\lambda}^2} \varrho_{1\lambda}^2 + \dots \right. \right. \\ \left. \left. \dots + 2 \frac{\partial^2 \psi_\lambda}{\partial n_{x\lambda} \partial n_{2\lambda}} \varrho_{1\lambda} \varrho_{2\lambda} + \dots \right\} \dots \right] \quad (1^a)$$

As conditions of equilibrium we now find

$$\frac{\partial \psi_\lambda}{\partial n_{x\lambda}} = f_x \quad \lambda \text{ from } 1 \text{ to } l \quad \dots \quad (7)$$

Further

$$\frac{1}{2} \sum_1^l \left\{ \frac{\partial^2 \psi_\lambda}{\partial n_{1\lambda}^2} \varrho_{1\lambda}^2 + \dots + 2 \frac{\partial^2 \psi_\lambda}{\partial n_{1\lambda} \partial n_{2\lambda}} \varrho_{1\lambda} \varrho_{2\lambda} + \dots \right\} > 0 \quad \dots \quad (8)$$

$$e^{-\frac{\Psi - \sum \Psi'_\lambda}{\Theta}} = \prod_1^k \prod_1^l \left\{ \frac{\omega(n_{1\lambda}, n_{x\lambda}, \dots, n_{x\lambda})}{n_{x\lambda}} \right\}^{n_{x\lambda}} \nu^{n_{x\lambda}} = e^{-\frac{\sum \psi_\lambda}{\Theta}} \nu^{\sum n_x}$$

the quantity  $\nu$  being an additive constant without any physical meaning;  $\sum \psi_\lambda$ , however, being connected with the difference of free energy from the zero state defined above.



The left member of this inequality consists of  $l$  terms, each of which relates to an element of volume  $v_\lambda$ . If we take into consideration that  $\psi_\lambda = \frac{v_\lambda}{v} \psi = \frac{1}{l} \psi$ , then it is seen that we have

$$\frac{\sigma^2 \psi_\lambda}{\partial n_{\lambda}^2} = \frac{1}{l} \frac{\partial^2 \psi}{\partial n_x^2}$$

and

$$\frac{\sigma^2 \psi_\lambda}{\partial n_{x\lambda} \partial n_{x'\lambda}} = \frac{1}{l} \frac{\sigma^2 \psi}{\partial n_x \partial n_{x'}} \dots \dots \dots (9)$$

The coefficients of all  $l$  forms therefore will be the same for all corresponding terms. In order to find the condition which is to be fulfilled by the coefficients in (8), we will consider the case

$$\varrho_{11} = -\varrho_{11'} \quad , \quad \varrho_{22} = -\varrho_{22'} \quad , \quad \varrho_{k\lambda} = -\varrho_{k\lambda'}$$

all other  $\varrho$ 's being 0. For this case we have for all possible values of the  $\varrho$ 's

$$\frac{\partial^2 \psi}{\partial n_1^2} \varrho_{11}^2 + 2 \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \varrho_{12} + \dots > 0,$$

only the index  $\lambda$  occurring.

The conditions, necessary for this to be true, are that 1. the discriminant  $\Delta$

$$\Delta = \begin{vmatrix} \frac{\partial^2 \psi}{\partial n_1 k} & \frac{\partial^2 \psi}{\partial n_1 \partial n_k} & \frac{\partial^2 \psi}{\partial n_1 \partial n_k} \\ \frac{\partial^2 \psi}{\partial n_1 \partial n_x} & \frac{\partial^2 \psi}{\partial n_x^2} & \frac{\partial^2 \psi}{\partial n_x \partial n_k} \\ \frac{\partial^2 \psi}{\partial n_1 \partial n_k} & \frac{\partial^2 \psi}{\partial n_k \partial n_k} & \frac{\partial^2 \psi}{\partial n_k^2} \end{vmatrix} > 0 \dots \dots \dots (10)$$

whereas the same must be true for the determinants originating from the discriminant if we successively omit the right-hand column and the last row. The conditions under which the system is really a maximum and therefore stable, agree with the well-known thermodynamical conditions of stability.

4. We are now able to determine the mean values of the squares of deviations  $\overline{\varrho^2_{x\lambda}}$  and of the products  $\overline{\varrho_{x\lambda} \varrho_{x'\lambda}}$ <sup>1)</sup>.

As is easily seen we have

$$\overline{\varrho^2_{x\lambda}} = \overline{\varrho^2_{x\lambda'}} \dots \dots \dots (11)$$

and

<sup>1)</sup> Mathematically speaking, our problem is one of correlate probability, my formulae agreeing with formulae Prof. J. C. KAPTEIJN communicated to me after I had solved this problem.

$$\overline{\varrho_{z\lambda} \varrho_{z'\lambda}} = \overline{\varrho_{z\lambda} \varrho_{z'\lambda}} \dots \dots \dots (11a)$$

To define  $\varrho^2_{11}$  e. g., we have

$$\begin{aligned} \overline{\varrho^2_{11}} &= \\ & \frac{\int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \varrho^2_{11} e^{-\frac{1}{2\Theta l} \sum_1^l \left\{ \frac{\partial^2 \psi}{\partial n_1^2} \varrho^2_{1\lambda} + \dots + 2 \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \varrho_{1\lambda} \varrho_{2\lambda} \dots \right\}} d\varrho_{11} \dots d\varrho_{kl}}{\int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} e^{-\frac{1}{2\Theta l} \sum_1^l \left\{ \frac{\partial^2 \psi}{\partial n_1^2} \varrho^2_{1\lambda} + \dots + 2 \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \varrho_{1\lambda} \varrho_{2\lambda} \dots \right\}} d\varrho_{11} \dots d\varrho_{kl}} \end{aligned}$$

Now,  $\sum \varrho_{1\lambda} = 0$ , etc. In order to take this into account in determining  $\varrho^2_{11}$ , we introduce new variables instead of  $\varrho_{12} \dots \varrho_{1\lambda} \dots \varrho_{1l}$ :

$$\varrho_{1\lambda} = \varrho'_{1\lambda} - \frac{1}{l-1} \varrho_{11} \quad \lambda \text{ from } 2 \text{ to } l.$$

Then we have

$$\sum_{\lambda=2}^l \varrho'_{1\lambda} = 0.$$

We also introduce for  $\varrho_{1\lambda} \dots \varrho_{z\lambda}$  new variables in a similar way. The exponents of the integral then can be expressed by

$$\begin{aligned} & \frac{1}{2l\Theta} \left\{ \varrho^2_{11} \frac{\partial^2 \psi}{\partial n_1^2} \left( 1 + \frac{1}{l-1} \right) + \right. \\ & \left. + 2 \varrho_{11} \varrho_{21} \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \left( 1 + \frac{1}{l-1} \right) \dots \varrho^2_{k1} \frac{\partial^2 \psi}{\partial n^2_k} \left( 1 + \frac{1}{l-1} \right) + C \right\}, \end{aligned}$$

where  $C$  is a quadratic function in the  $\varrho'_{1\lambda} \varrho'_{2\lambda}$  ( $\lambda$  2 to  $l$ ).

Now, taking into account the conditions  $\sum \varrho'_{1\lambda} = 0$ , we can integrate with respect to the variables  $\varrho'_{z\lambda}$  i.e. with respect to the elements  $2 \dots \lambda \dots l$ ; the result in the numerator being cancelled by that in the denominator. In this way we find

$$\begin{aligned} \overline{\varrho^2_{11}} &= \frac{\int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \varrho^2_{11} e^{-\frac{1}{2(l-1)\Theta} \left\{ \varrho^2_{11} \frac{\partial^2 \psi}{\partial n_1^2} + \dots + 2 \varrho_{11} \varrho_{21} \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \right\}} d\varrho_{11} \dots d\varrho_{kl}}{\int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} e^{-\frac{1}{2(l-1)\Theta} \left\{ \varrho^2_{11} \frac{\partial^2 \psi}{\partial n_1^2} + \dots + 2 \varrho_{11} \varrho_{21} \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \right\}} d\varrho_{11} \dots d\varrho_{kl}} \end{aligned}$$

According to a well-known theorem (comp. GIBBS El. Pr. in Stat. Mech. p. 205) we have

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\frac{1}{2\Theta(l-1)} \left\{ \frac{\partial^2 \psi}{\partial n_1^2} \varrho_{11}^2 + \dots + 2 \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \varrho_{11} \varrho_{21} \dots \right\}} \\ (2\pi(l-1)\Theta)^{\frac{k}{2}} \frac{1}{\Delta^{1/2}}, \dots \dots \dots (13).$$

where  $\Delta$  is the determinant defined by (10). Differentiating the logarithm of (13) with respect to  $\frac{\partial^2 \psi}{\partial n_1^2}$ , we find

$$\overline{\varrho_{11}^2} = (l-1)\Theta \frac{\Delta_{11}}{\Delta}$$

and in general

$$\overline{\varrho_{x\lambda}^2} = (l-1)\Theta \frac{\Delta_{xx}}{\Delta} \dots \dots \dots (14)$$

whereas at the same time we find

$$\overline{\varrho_{x\lambda} \varrho_{x'\lambda}} = (l-1)\Theta \frac{\Delta_{xx'}}{\Delta} \dots \dots \dots (14a)$$

The quantities  $\Delta_{xx}$  and  $\Delta_{xx'}$  represent in the usual way the minor determinants in  $\Delta$ .

If  $l$  is great with respect to 1, then we can replace  $l-1$  by  $l$ , and this quantity by  $\frac{V}{V_\lambda}$ , and keeping in mind that  $\Theta = \frac{RT}{N}$ , we have

$$\overline{\varrho_{x\lambda}^2} = \frac{RT}{N} \frac{V}{V_\lambda} \frac{\Delta_{xx}}{\Delta} \dots \dots \dots (15)$$

$$\overline{\varrho_{x\lambda} \varrho_{x'\lambda}} = \frac{RT}{N} \frac{V}{V_\lambda} \frac{\Delta_{xx'}}{\Delta} \dots \dots \dots (15a)$$

where  $\varrho_x$  and  $\varrho_{x'}$  are used to denote  $\varrho_{x\lambda}$  and  $\varrho_{x'\lambda}$ .

We can still modify these equations by introducing the free energy for the unit of volume filled with the given density. As  $\psi = V\bar{\psi}$ , we obtain  $\Delta = V^k \bar{\Delta}$  ( $\bar{\Delta}$  then relating to the determinant (10) for  $\bar{\psi}$ ).  $\Delta_{xx} = V^{k-1} \bar{\Delta}_{xx}$  etc. and we find

$$\overline{\varrho_x^2} = \frac{1}{V_\lambda} \frac{RT}{N} \frac{\bar{\Delta}_{xx}}{\bar{\Delta}},$$

and

$$\overline{\varrho_x \varrho_{x'}} = \frac{1}{V_\lambda} \frac{RT}{N} \frac{\bar{\Delta}_{xx'}}{\bar{\Delta}}.$$

Taking into account that  $\tau_{x\lambda}$ , being the deviation from  $n_{x\lambda}$ , amounts to  $V_\lambda \varrho_{x\lambda}$ , we find

$$\overline{\tau_{\lambda}^2} = V_{\lambda} \frac{RT}{N} \frac{\overline{\Delta_{\lambda\lambda}}}{\Delta}.$$

For the frequency  $\zeta_{\Delta}$  of a deviating system we have

$$\zeta_{\Delta} = \zeta_0 e^{-\frac{1}{2\theta l} \sum_1^l \left\{ \frac{\partial^2 \psi}{\partial n_1^2} \varrho_1^2 + \dots + 2 \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \varrho_1 \varrho_2 + \dots \right\}}.$$

The probability of a system is proportional to  $\zeta_{\Delta}$ , and the logarithm of thus defined probability is, as I formerly showed, equivalent to the entropy <sup>1)</sup>. The difference of entropy of the stationary and the deviating state therefore amounts to

$$-\frac{R}{2N\theta l} \sum_1^l \left\{ \frac{\partial^2 \psi}{\partial n_1^2} \varrho_1^2 + \dots \right\}$$

or

$$-\frac{1}{2Tl} \sum_1^l \left\{ \frac{\partial^2 \psi}{\partial n_1^2} \varrho_1^2 + \dots + 2 \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \varrho_1 \varrho_2 \dots \right\}$$

The energy taken by the transition can therefore be expressed by

$$-\frac{1}{2l} \sum_1^l \left\{ \frac{\partial^2 \psi}{\partial n_1^2} \varrho_1^2 + \dots + 2 \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \varrho_1 \varrho_2 \dots \right\}$$

The mean value of this energy is

$$-\frac{RT}{2N} l.$$

the absolute value being

$$\begin{aligned} \frac{1}{2} \sum \left\{ \overline{\varrho_1^2} \frac{\partial^2 \psi}{\partial n_1^2} + 2 \overline{\varrho_1 \varrho_2} \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \dots \right\} = \\ \frac{RT}{2N} \frac{l}{\Delta} \sum \left\{ \Delta_{11} \frac{\partial^2 \psi}{\partial n_1^2} + \dots + 2 \Delta_{12} \frac{\partial^2 \psi}{\partial n_1 \partial n_2} \dots \right\} = \\ \frac{RT}{2N} l \end{aligned}$$

This result agrees with that found on p. 852 of the quoted communication.

5. If  $\chi$  is some observable quantity depending on the densities  $n_{1\lambda} \dots n_{z\lambda} \dots n_{z\lambda}$  in the elements  $V_{\lambda}$ , then with the help of the given formula we can easily calculate the probability of a set of values  $\chi_1 \dots \chi_{\lambda} \dots \chi_l$ , and the mean squares of deviations. For  $\chi_{\Delta}$  we have (limiting ourselves for a moment to a single element and therefore omitting the index)

$$\chi_{\Delta} - \chi_0 = \frac{\partial \chi}{\partial n_1} \varrho_1 + \frac{\partial \chi}{\partial n_z} \varrho_z + \frac{\partial \chi}{\partial n_k} \varrho_k$$

and so we have

<sup>1)</sup> Comp. Entropy and probability, Proceedings 1912 p. 840.

$$\overline{(\chi_\Delta - \chi_0)^2} = \bar{\xi}^2 = \left(\frac{\partial \chi}{\partial n_1}\right)^2 \overline{q_1^2} + 2 \frac{\partial \chi}{\partial n_1} \frac{\partial \chi}{\partial n_2} \overline{q_1 q_2} + \dots$$

From which it appears, that

$$\overline{(\chi_\Delta - \chi_0)^2} = \bar{\xi}^2 = \frac{V}{V_\lambda} \frac{RT}{N} \frac{1}{\Delta} \left\{ \left(\frac{\partial \chi}{\partial n_1}\right)^2 \Delta_{11} + \dots + 2 \frac{\partial \chi}{\partial n_1} \frac{\partial \chi}{\partial n_2} \Delta_{12} \dots \right\}$$

which may also be written

$$\bar{\xi}^2 = - \frac{1}{\Delta} \frac{RT}{N} \frac{V}{V_\lambda} D. \quad \dots \quad (16)$$

In the formula  $D$  represents the determinant

$$D = \begin{vmatrix} 0 & \frac{\partial \chi}{\partial n_1} & \frac{\partial \chi}{\partial n_x} & \frac{\partial \chi}{\partial n_k} \\ \frac{\partial \chi}{\partial n_1} & \frac{\partial^2 \psi}{\partial n_1^2} & \frac{\partial^2 \psi}{\partial n_1 \partial n_x} & \frac{\partial^2 \psi}{\partial n_1 \partial n_k} \\ \frac{\partial \chi}{\partial n_x} & \frac{\partial^2 \psi}{\partial n_1 \partial n_x} & \frac{\partial^2 \psi}{\partial n_x^2} & \frac{\partial^2 \psi}{\partial n_x \partial n_k} \\ \frac{\partial \chi}{\partial n_k} & \frac{\partial^2 \psi}{\partial n_1 \partial n_k} & \frac{\partial^2 \psi}{\partial n_x \partial n_k} & \frac{\partial^2 \psi}{\partial n_k^2} \end{vmatrix}.$$

With the help of the given values of  $\xi$ , and of transformations which to some degree answer to those already performed, we can show that the probability of a system in which the deviations of  $\chi$ ,  $\xi_1 \dots \xi_\lambda \dots \xi_l$ , are between  $\xi_\lambda$  and  $\xi_\lambda + d\xi_\lambda$ , amounts to

$$W_\xi^{\xi+d\xi} = W_0 e^{-\frac{\Delta}{2l\Theta D} (\xi_1^2 + \xi_\lambda^2 + \xi_l^2)} d\xi_1 \dots d\xi_\lambda \dots d\xi_l.$$

For  $\Theta \log \frac{W_\xi}{W_0}$  we therefore have

$$-\frac{\Delta}{2lD} (\xi_1^2 + \dots \xi_\lambda^2 + \dots \xi_l^2).$$

The mean value of this quantity is

$$\Theta \log \frac{W_\xi}{W_0} = \frac{R}{N} T \log \frac{W}{W_0} = + \frac{\Delta}{2lD} \bar{\xi}^2 = - \frac{lRT}{2N}.$$

It appears from this, that  $\Theta \log \frac{W_\xi}{W_{\xi_0}} = \Theta \log \frac{W_\rho}{W_{\rho_0}}$ . The probability of a state defined with the help of the quantity  $\chi$  therefore also agrees with the entropy, at least as far as the mean values which generally are only of importance, are concerned. Instead of the  $k$  partial densities also the function  $\chi$  of them can serve therefore to define the entropy of deviating systems. In the quoted communication

on entropy and probability this has been shown for arbitrary observable parameters. The mean energy of deviation did not depend on the nature of the parameters, but on their number only; and also in the case considered it is not the partial density in the elements but only the number of elements discernible for observation which plays a part.

Groningen, April 1912.

**Mathematics.** — “*Calculus rationum.*” (2<sup>nd</sup> Part). By Dr. G. DE VRIES. (Communicated by Prof. JAN DE VRIES.)  
(Communicated in the meeting of March 30, 1912).

§ 16. If in the following remarkable root

$$\frac{{}^n(u) \Big| u}{{}^n(v) \Big| v} = \frac{{}^n}{1} [{}^{n-1}p(u), p^{-1}(v)]$$

we put  $v = u$ , the left member assumes the form  $1^\infty$  apparently indefinite; the right member becomes  ${}^{n-1}(u)^n$ . Introducing the sign  $R$  for the ratio of two values of a variable lying infinitely close together, we can write:

$$Ry \mid Rx = {}^{n-1}(x)^n \text{ for } y = {}^n(x).$$

This is a mutual root of two ratios lying infinitely close to unity. If it is now even obvious to introduce in agreement to the preceding a *rational radix* as measure for the field of ratio, then the significance of a mutual root of exponential numbers is strengthened by the fact that of the following forms

$$\lim_{\infty} \frac{a^x}{b^x} ; \quad \lim_{\infty} a^x \mid b^x;$$

the latter has no sense, the former has.

If for the comparison of two variables a third is introduced as independent variable and if we then put

$$x = e^{f(z)} \quad ; \quad y = e^{F(z)};$$

then from this can be deduced:

$$e^{f'(z)} = \lim \sqrt[\Delta z]{1 + \frac{\Delta x}{x}} \quad ; \quad e^{F'(z)} = \lim \sqrt[\Delta z]{1 + \frac{\Delta y}{y}}.$$

When joining these we find that  $\Delta z$  disappears when one of the mutual roots is calculated.

$$e^{F'(z)} : f'(z) = \lim \left( 1 + \frac{\Delta y}{y} \right) \Big| \left( 1 + \frac{\Delta x}{x} \right) = \lim \sqrt[\Delta Lx]{\frac{y + \Delta y}{y}}.$$

Introducing for the rational radix the sign  $\surd R$

$$\sqrt[R]{y} = Ry \mid Rx = e^{\frac{dLy}{dLx}}.$$

Without causing confusion we can omit for two variables the root exponent, and when repeating the operation we can write  $\sqrt[R]{R}$ ,  $\sqrt[R]{R} \dots$

For the rational defined in § 6 the above mentioned quantity is constant, just as the differential coefficient of the logarithms is.

§ 17. General rules for the rationalising are easy to fix; thus

$$\sqrt[R]{uv} = \sqrt[R]{u} \cdot \sqrt[R]{v};$$

$$\sqrt[R]{u,v} = (v, \sqrt[R]{u}) \cdot (u, \sqrt[R]{v}) ; \sqrt[R]{u|v} = \{(v, \sqrt[R]{u}) ; (u, \sqrt[R]{v})\} |^2(v);$$

$$\sqrt[R]{u+v} = \sqrt[R]{(\sqrt[R]{u})^{u+v} \cdot (\sqrt[R]{v})^v};$$

$$\sqrt[R]{x} = e | \sqrt[R]{y}.$$

Then the following rational radices often appear:

$$\sqrt[R]{R^n(x)} = {}^{n-1}(x)^n;$$

$$\sqrt[R]{RLx} = e | x;$$

$$\sqrt[R]{R x^x} = (ex)^x;$$

$$\sqrt[R]{R sr x} = cr x ; \sqrt[R]{R cr x} = (sr x)^{-1};$$

$$\sqrt[R]{R tr x} = e \cdot {}^2(tr x);$$

$$\sqrt[R]{R \tan^{-1} r x} = e | e \cdot {}^2(x);$$

where we are reminded of the meaning of  $tr$ , mentioned in § 8;  $\tan^{-1} r$  represents here the opposite.

We mention as peculiarity that the exponential function remains unaltered in this operation.

$$\sqrt[R]{R a^x} = a^x.$$

§ 18. As starting point for the development in series of the product we choose:

$$e^x = e \prod_1^{\infty} \sqrt[R]{p(x)},$$

which formula immediately follows out of

$$x = e^{Lx} = 1 + \sum_1^{\infty} \frac{L^p x}{p!}.$$

In a general way we can also deduce the analogon of MACLAURIN'S series:

$$y = y_1 \prod_1^{\infty} (\sqrt[R]{p(x)}, \sqrt[R]{R y_1}); \dots \dots \dots (I)$$

in which the index 1 refers to the values of the function and derivatives for 1. If the ratio in which the independent variable increases becomes  $r_x$ , if the corresponding accretion of ratio of the dependent

variable is called  $r_y$ , then the series corresponding to TAYLOR'S series is:

$$y r_y = f(x r_x) = f(x) \prod_1^{\infty} [\sqrt[p]{p(r_x)}, \sqrt[p]{R f(x)}]. \quad (II)$$

It can be of service in geometrical investigations of particular points.

Whilst now  $x_x$  cannot be developed in a series of sum, it is possible to find a series of products:

$$x_x = x \prod_1^{\infty} \sqrt[p+1]{p} (x).$$

For the following development exists the limitation:  $\frac{e}{1} < x < e$ .

$$L(ex) = \prod_1^{\infty} \sqrt[p]{p(x)^{-1}}^{p-1}.$$

§ 19. For a maximum or minimum holds:

$$\sqrt{Ry} = 1.$$

From series II (§ 18) follows, that in the immediate vicinity of the point the change of  $y$  depends on the factor:

$$\sqrt[2]{r_x}, \sqrt[2]{Ry}$$

whose first efficient is always greater than *one*, so that the second efficient decides whether in the point there is a maximum or a minimum.

For the second rational radix we find deduced:

$$\sqrt[2]{Ry} = \sqrt[2]{e^{x^2 y''}} \cdot \sqrt{Ry} : \sqrt[2]{Ry}.$$

From this ensues as condition of an inflectional point

$$\sqrt[2]{Ry} = \sqrt{Ry} : \sqrt[2]{Ry}$$

A rational inflectional point is characterized by

$$\sqrt[2]{Ry} = 1.$$

In such a point the curve has with the touching rational 3 points in common. That now the two curves osculate each other follows easily from the equation of the rational (§ 7).

$$y'' = \frac{y}{x^2} \lambda(\lambda-1) \quad ; \quad e^x = \sqrt{Ry} \quad ; \quad \text{so} : \sqrt[2]{e^{x^2 y''}} = \sqrt[2]{Ry} : \sqrt{Ry} ;$$

so that the preceding condition is satisfied.

The rational of contact in  $(x_1, y_1)$  is given by:

$$\frac{y}{y_1} = \frac{x}{x_1}, \sqrt{Ry_1}.$$



When asymptotes (rationals) are at hand, the following formulae for  $x_1$  or  $y_1$  infinite or zero tend to a definite value

$$\lambda = \sqrt{Ry_1} \text{ and } m = y_1 : x_1, \sqrt{Ry_1}.$$

By rational subtangent of a curve we understand the ratio of the absciss to the absciss of the point of intersection of the rational of contact with the axis  $OX_1$ ; it is given by

$$y|\sqrt{Ry}.$$

The envelope of a series of curves is found in the same way as in the differential calculus.

§ 20. There exists an integrating operation which reduces the functions obtained by means of rationalization to the original ones. It can be regarded as the limiting product of mutual powers, of which one of the efficient lies infinitely close to unity. It shall be named *multiplical(-potence)*; its form is:

$$\lim \Pi \left( y, \left( 1 + \frac{\Delta x}{x} \right) \right) = Py^{dLx} = e^{\int Ly^{dLx}}.$$

For an indefinite multiplical a constant factor must be added; e.g.

$$P^n(x)^{dLx} = c\sqrt[n+1]{(x)}$$

$$P(e|x)^{dLx} = L(c, x)$$

$$P_x x^{dLx} = c \left( \frac{x}{e} \right)^x$$

$$P(cr.x)^{dLx} = c \cdot sr.x.$$

For definite multiplicals the constant disappears; we have to take into consideration the following rules:

$$\frac{3}{1} P_y^{dLx} = \frac{2}{1} P_y^{dLx} \cdot \frac{3}{2} P_y^{dLx} \dots \dots \dots (I)$$

$$\frac{x_2}{x_1} P_y^{dLx} = \frac{y_2, x_2}{y_1, x_1} : \frac{y_2}{y_1} P_x^{dLy} \dots \dots \dots (II)$$

§ 21. A rational is determined by two points: the director exponent  $\lambda = tg\varphi$  follows out of:

$$\frac{y_2}{y_1} = \left( \frac{x_2}{x_1} \right)^\lambda.$$

If now  $(x_0, y_0)$  is a point out of which the rational distance ( $\varrho$ ) is measured, then holds

$$\sqrt{\frac{\cos \varphi}{x_0}} x := \sqrt{\frac{\sin \varphi}{y_0}} y = \varrho, \text{ and } \left( \frac{x}{x_0} \right)^\lambda \cdot \left( \frac{y}{y_0} \right) = {}^2(\varrho).$$

For the ratio of two such distances on the line we find:

$$\sqrt{\frac{\cos \varphi}{x_1} \frac{x_2}{y_1}} = \sqrt{\frac{\sin \varphi}{y_1} \frac{y_2}{x_1}} = \frac{\rho_2}{\rho_1} = \rho_{1.2}.$$

This can also be represented by a definite multiplical, of which the indefinite form is:

$$S = e^{\int \sqrt{(dLx)^2 + (dLj)^2}} = \lim_{\frac{2}{1}} \Pi \left[ \left( 1 + \frac{\Delta x}{x} \right) \cdot \left( 1 + \frac{\Delta y}{y} \right) \right].$$

For the rational this becomes:

$$S = e^{\int_1^2 \sqrt{1+\lambda^2} dLx} = [x^{\sec \varphi}]_1^2 = \frac{\rho_2}{\rho_1}.$$

It is obvious that we can give to  $S$  the name of *rational length of arc*. It represents therefore for an arbitrary curve the limit of the product of the rational distances taken from point to point; where thus  $\sqrt{R}$  continually changes into the following form:

$$S = P \int_1^2 [e^{\lambda} (\sqrt{Ry})] dLx.$$

For a line parallel to the  $X$ -axis this has the simplest form, viz.:

$$S = \frac{x_2}{x_1}$$

The multiplical mentioned in § 20 then becomes if  $y = y_0$  (constant):

$$P y_0 dLx = \frac{x_2}{x_1}, y_0.$$

This represents the rational area of the rectangle determined by the above mentioned coordinates. For the rational trapezium bounded by  $y_1$ ,  $y_2$  and a rational we have

$$P y dLx = \frac{x_2}{x_1}, \sqrt{y_1 y_2} = \frac{x_2}{x_1}, y_0,$$

when  $y_0$  is the mean proportional. We can also take that multiplical as a power of a ratio of area, when we write:

$$\left( \frac{x_2 y_0}{x_1 y_0} \right)^{Ly_0}.$$

Also for an arbitrary curve that multiplical will be called the rational area; it is entirely determined by the limiting coordinates.

§ 22. From the notion "rational area" is deduced that of "rational angle" (already mentioned in § 8). In fig. 8 the rational  $MB$  determines with  $MA$  and the logarithmic circle a sector whose rational area is going to be calculated. The multiplical extended over  $ABDM$  is

$$\int_1^x \left[ \frac{1}{2} \frac{r^2}{x^2} \right]^{dLx} = \mathcal{V} \left[ (x, y) \cdot \left( r^2, e^{\frac{\pi}{2} - \varphi} \right) \right],$$

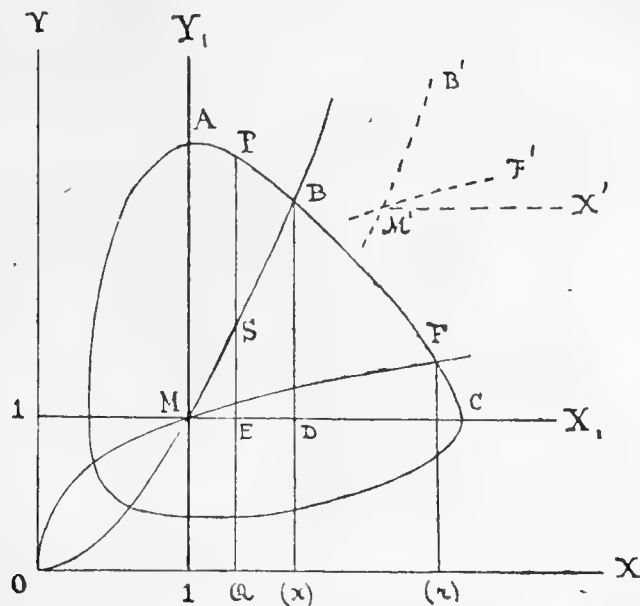


Fig. 8.

if namely we put

$$\varphi = \cos^{-1} \frac{Lx}{Lr}.$$

It is evident from the preceding that the first factor is the rational area of  $\triangle MBD$ . With a view to the equation

$$\frac{PQ}{EQ} = \frac{PQ}{SQ} \times \frac{SQ}{EQ},$$

the 2<sup>nd</sup> factor will indicate the rational area of  $\triangle MBP$ .

$$\lim \Pi \left( \frac{PQ}{SQ} \right)^{\Delta Lx} = \left( e^{\frac{\pi}{2}} : e^{\varphi} \right), \mathcal{V}^2(r)$$

Extended over the quadrant  $AMC$  the multiplical becomes:

$$e^{\frac{\pi}{2}}, \mathcal{V}^2(r) = {}^2(\mathcal{V}r)^{\pi};$$

so that holds for sector  $BMC$ :

$$\mathcal{V}^2(r)^{\text{arc } \cos \frac{Lx}{Lr}} = \mathcal{V}^2(r), u;$$

$u$  is the "rational angle" mentioned before. For this holds:

$$u = e; \text{tr } u = e^{\text{tg } Lu} = y | x;$$

furthermore, we must notice:

$$u = \tan^{-1} r (y | x) = \cos^{-1} r (x | r) = \sin^{-1} r (y | r).$$

If the radius of the logarithmic circle is  $e$  then holds:

$$P(BMC) = \mathcal{V}u.$$

It is easy to see that the multiplical over  $MBF$  is:

$$P(BMF) = P(BMC) : P(FMC) = \sqrt{\frac{u_2}{u_1}} = \sqrt{u_{1,2}}$$

The *rational angle* comprised between two rational radii through  $M$  is the second power of the rational area of the figure enclosed by the radii and the logarithmic circle with radius  $e$  and centre  $M$ . For the rational area of a logarithmic circle holds:

$${}^2(r) \pi$$

For rational length of chord and circumference we find:

$$r, u \text{ and } r^{2\pi}$$

By two rationals of centre sectors are cut out of concentric logarithmic circles whose rational areae form with the second gradations of the radii a logarithmic proportion. Such figures are in rational sense congruent.

§ 23. Besides the rational circle functions the rational hyperbolic functions are of importance. Just as in difference geometry they appear in the simplest way by the consideration of areae of the logarithmic equilateral hyperbola with equation:

$${}^2(x) : {}^2(y) = {}^2(a).$$

Side by side with the current notation of the ordinary functions we can write:

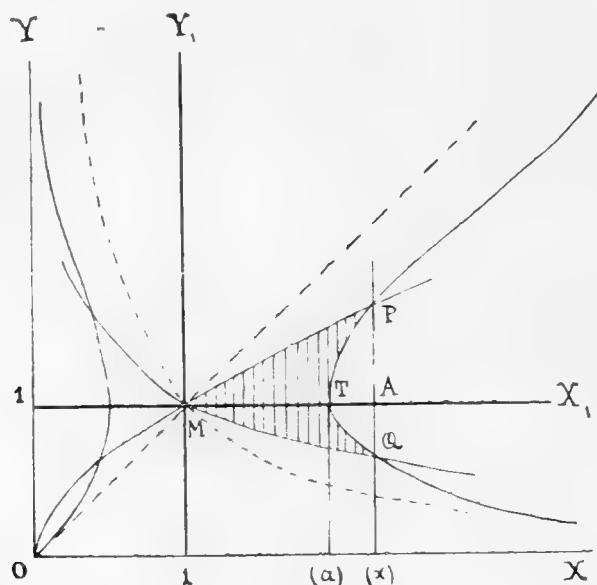


Fig. 9.

$$ch Lu = \frac{1}{2} \left( u + \frac{1}{u} \right) ; \quad sh Lu = \frac{1}{2} \left( u - \frac{1}{u} \right).$$

If  $a$  is again the parameter the area of a sector is given by:

$$I = a^2 L \sqrt{u} \quad \text{or} \quad u = \frac{2I}{a^2}$$

In connection with this holds the definition for the "rational functions":

$$\text{chr } u = e^{hLu} = (\sqrt{e})^{u + \frac{1}{u}} ; \quad \text{shr } u = e^{shLu} = (\sqrt{e})^{u - \frac{1}{u}} \text{ etc.}$$

By the substitution

$$x = a, \text{ chr } u ; \quad y = a, \text{ shr } u$$

the rational area of  $TPA$  (fig. 9) is determined.

$$\frac{x}{a} P_y dLx = \sqrt{x, y} : \left( \sqrt{^2(a)}, \frac{Lxy}{La} \right).$$

Now the numerator of the 2<sup>nd</sup> member again represents the rational area of  $PMA$  so that the denominator is that quantity for  $PMT$ . The argument of the function is therefore determined by the rational area of sector  $MPTQ$ . Simpler are the relations for  $a = e$ ; then

$$\frac{x}{e} P_y dLx = \sqrt{x, y} : Lxy ; \quad u = Lxy ; \quad \frac{1}{u} = L \frac{x}{y} ;$$

out of which again the following relations are formed:

$$\text{chr } u \times \text{shr } u = e^u ; \quad \text{chr } u : \text{shr } u = \sqrt[2]{e}$$

Development of series furnishes

$$\text{chr } u = e \prod_1^{\infty} \sqrt[2]{2p}(u) ; \quad \text{shr } u = \prod_1^{\infty} \frac{(2p-1)}{2p} \sqrt[2]{2p-1}(u).$$

§ 24. If the multiplical is calculated for the logarithmic equilateral hyperbola in the equation on the asymptotes, then these functions appear again.

$$x, y = ^2(a) ; \quad \frac{x}{a} P_y dLx = \frac{Lx}{La}, ^2(a) ;$$

$a = e$  leads to a new form for the logarithm:

$$Lx = \frac{x}{e} P_y dLx = \frac{x}{e} (e \setminus x) dLx.$$

If this (shortened by  $P_x$ ) is introduced as argument, then

$$\text{chr } P_x = \sqrt[2]{xy} ; \quad \text{shr } P_x = \sqrt[2]{\frac{x}{y}}$$

from which ensue easily the properties; as i.a.:

$$\text{chr } P_x^2 = ^2(\text{chr } P_x) \cdot ^2(\text{shr } P_x).$$

The above mentioned curve forms a part of the elementary curves in the rootfield. The general equation of these "gradation curves" is:

$$y = m, ^2(x)$$

In the supposition  $\lambda > 1$  we find

$$\frac{x}{1} \frac{y^{dLx}}{1} = \sqrt[\lambda+1]{x, y} ; \quad \frac{y}{1} \frac{PxdLy}{1} = \sqrt[\lambda+1]{x^\lambda, y}$$

So that we find, calling the multiplicals for short  $P_x$  and  $P_y$ :

$$P_y | P_x = e^\lambda.$$

The gradation curves divide the rootfield in such a way that the mutual root of the rational areae measured along the curve has a constant value.

§ 25. An equation, in which besides the variables also rational radices or the rationals of the functions appear, is called a rational equation. In some cases equations can be solved in which besides the above mentioned quantities still differential coefficients appear.

I. Required is the curve for which the rational subtangent is constant. The equation runs:

$$y | \sqrt{Ry} = a.$$

In succession we write:

$$\begin{aligned} r_x | a &= r_y | y \\ P(e|a)^{dLx} &= P(e|y)^{dLy} \\ x, (e|a) &= L(c, y) \\ y &= e^{x|a|c} \end{aligned}$$

This represents the logarithmic curve of arbitrary order.

II. To find the curve for which the rational radix is proportional to the differential coefficient. Out of the condition:

$$\sqrt{Ry} = p \cdot \frac{dy}{dx}$$

follows as answer:

$$y = e^{cx} : cp \text{ and } y = \frac{e}{p} x.$$

The last answer is the singular solution and those which by means of an integrating power can be reduced to such. Fartheron the rationalisation under the multiplicative sign for which it is easy to compose the formula.

§ 26. Some of the above mentioned formulae can be extended, as i.a. the 3<sup>rd</sup> formula of § 17.

$$\sqrt{R} \sum_1^n (u_p) = \sqrt{\prod_1^n [\sqrt{R}(u_p)]^{u_p}}$$

If the sum passes into an integral, this formula becomes :

$$\sphericalangle R \int y dx = e^{xy} | e^{\int y dx}.$$

From the preceding we can gather that in all respects the field of difference with the corresponding functions represents the logarithm of the field of difference with the corresponding rational functions. This can be carried further consistently as regards angles and areas. By means of a simple "transformator" we pass from one field to another, thus we arrive by substitution of

$$x = e^X; \quad y = e^Y \text{ and } a = e^A$$

in the equation of the logarithmic hyperbola

$$x, y = {}^2(a) \quad ; \quad XY = A^2,$$

at that of the ordinary hyperbola.

Also ambiguous fields can be considered; i. a. the "semi-rational field", in which the absciss ascends with differences, whilst the ordinate changes by ratios. Thus the consideration of the semimultiplical:

$$\underset{0}{\overset{n}{P}} x dx = \left( \frac{n}{e} \right)^n$$

has led me to the equation:

$$\lim_{\infty} (p : \sphericalangle p!) = e;$$

one thing as well as the other in connection with the "geometrical-arithmetical series".

§ 27. The rational in fig. 8 brought through a point  $M'(a, b)$  equidistant with  $MB$ , for which we write  $M'B' || MB$ , has as equation:

$$\frac{y}{b} = \left( \frac{x}{a} \right)^\lambda \text{ or } \frac{y}{b} \left| \frac{x}{a} = e^\lambda.$$

If a logarithmic circle is drawn having  $M'$  as centre,  $r$  as radius, then the rational area of the sector, described by  $M'B'$  and  $M'X'$  ( $||MX_1$ ) proves to be:

$$\sphericalangle^2(r), \tan^{-1} r \left( \frac{y}{b} \left| \frac{x}{a} \right. \right);$$

hence the rational angle is

$$\tan^{-1} r e^\lambda.$$

This is as large as the one between  $MB$  and  $MC$ , the equation of  $MB$  being

$$y \left| x = e^\lambda.$$

So we can also see, that:

$$\angle B', M', F' = \angle B, M, F$$

if namely  $M'F' || MF$  and the separation by means of the commas indicates the rational angle. In *one* formula we write

$$u'_2 : u'_1 = u_2 : u_1.$$

(These angles must not be confounded with those of the tangents).

Three rationals determine a rational triangle the sides of which are the rational distances of the points of intersection. These shall be represented as follows:

$$P_3 = P_1, P_2 = \lambda^2 \left( \frac{x_2}{x_1} \right) \cdot \left( \frac{y_2}{y_1} \right), \text{ etc.}$$

By interchange of the letters the value is reversed.

Thus holds:

$$P_2, P_1 = (P_1, P_2)^{-1},$$

likewise

$$P, P = 1.$$

If the angles are indicated by  $u_1, u_2$  and  $u_3$  and if equidistant rationals are drawn through the vertices, e. g.  $P_1, Q || P_3, P_2,$

$$\angle P_2, P_1, Q = u_2 \quad ; \quad \angle O, P_1, P_3 = u_3.$$

As these are completed by  $u_1$  to a rational stretched angle, we find that:

$$u_1 u_2 u_3 = e^\pi.$$

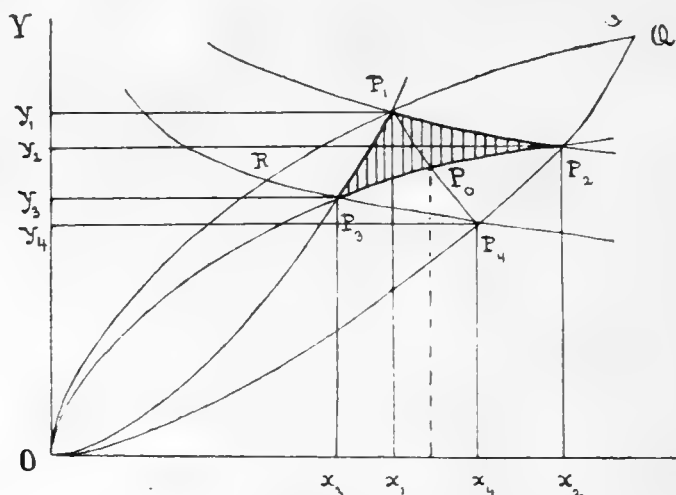


Fig. 10.

A rational right angle is the root out of a rational stretched angle. If  $\lambda_1$  and  $\lambda_2$  are the director exponents of two rationals, then holds for the rational angle formed by these:

$$tr u = (e^{\lambda_2} : e^{\lambda_1}) | e \cdot (e^{\lambda_2}, e^{\lambda_1});$$

so that the condition for a rational angle becomes:

$$1 + \lambda_1 \lambda_2 = 0.$$



§ 28. To get a good insight in the significance of the field of ratio it is important to name some more theorems out of rational planimetry.

The rational area of triangle  $P_1, P_2, P_3$  is given in:

$$\frac{1}{3} P(m_2, x_2) \cdot \frac{dLx}{1} \frac{2}{3} P(m_3, x_3) : \frac{dLx}{3} \frac{2}{3} P(m_1, x_1) .$$

After a few reductions we find the following symmetrical form:

$$\Delta = \frac{2}{1} P \times \frac{3}{2} P \times \frac{1}{3} P = \sphericalangle \left( y_1, \frac{x_2}{x_3} \right) \cdot \left( y_2, \frac{x_3}{x_1} \right) \cdot \left( y_3, \frac{x_1}{x_2} \right).$$

In case  $P_3$  coincides with  $M(1,1)$  the form becomes:

$$\sphericalangle (y_1, x_2) : (y_2, x_1).$$

If three points lie on one rational, then its value becomes *one*, as is easy to see.

For the rational area  $P_0$  of the rational parallelogram (fig. 10) holds:

$$P_0 = \frac{1}{3} \frac{2}{1} P : \frac{4}{3} \frac{2}{4} P = \frac{2}{1} \frac{4}{2} \frac{3}{4} \frac{1}{3} P = (P : P) : (P : P)$$

in which for short for the multiplicals one letter is taken, e.g.  $\frac{1}{3} P$  for area  $(P_3, P_1, x_1, x_3)$ . Out of the equidistance of the sides follows immediately:

$$x_1 : x_2 = x_3 : x_4 \quad ; \quad y_1 : y_2 = y_3 : y_4 ;$$

so that two opposite rational sides are equal:

$$P_1, P_2 = \sphericalangle \left( \frac{x_2}{x_1} \right)^2 \left( \frac{y_2}{y_1} \right) = \sphericalangle \left( \frac{x_4}{x_3} \right)^2 \left( \frac{y_4}{y_3} \right) = P_3, P_4.$$

The analogon of the theorem of PYTHAGORAS can be deduced in the simplest way out of the equation of the logarithmic circle. For a rational rectangular triangle placed arbitrarily we have but to apply revolution about the axis (see § 15). Thus we find also easily the rational area of a triangle, which is the root out of the mutual power of a rational side and the rational height let down out of the third vertex on to it. The considerations of the rational vector-analysis lead in a shorter manner than the ways indicated here to the results required.

A word or two must still be said about polar coordinates. The equation of the rational becomes:

$$\varrho, cr \frac{u}{u_0} = \varrho_0,$$

when  $\varrho$  is the rational distance  $M(1,1)$  to the point of the line and

$u$  the corresponding rational angle, whilst  $\varrho_0$  and  $u_0$  relate to the perpendicular-rational out of  $M$ .

For the rational area of a logarithmic circle sector we find:

$$\int_{u_0}^u P \mathcal{V}^2(\varrho) dLu = \mathcal{V}^2(\varrho) \frac{u}{u_0}.$$

The rational, i.e. the multiplical over an infinitesimal sector of a logarithmic circle is therefore:

$$\mathcal{V}^2(\varrho) dLu.$$

Applied to the triangle  $M, P_1, P_2$  mentioned in § 28 we find that multiplical integration furnishes, when  $P_1, P_2, P_3$  is a right line:

$$\mathcal{V}^2(\varrho_1), tr u_3 = \mathcal{V}^2(\varrho_1), (\varrho_3 | \varrho_1) = \mathcal{V} \varrho_1 \varrho_3.$$

§ 29. Fig. 11 can give us a good idea of two equal skew ratios. If  $P_1$  and  $P_2$  are points of a rational, we then find two points with equal rational distance on an equidistant rational by transferring successively the abscissae and ordinates or reversely. So here is

$$x_1 : x_2 = x_3 : x_4 \quad ; \quad y_1 : y_2 = y_3 : y_4,$$

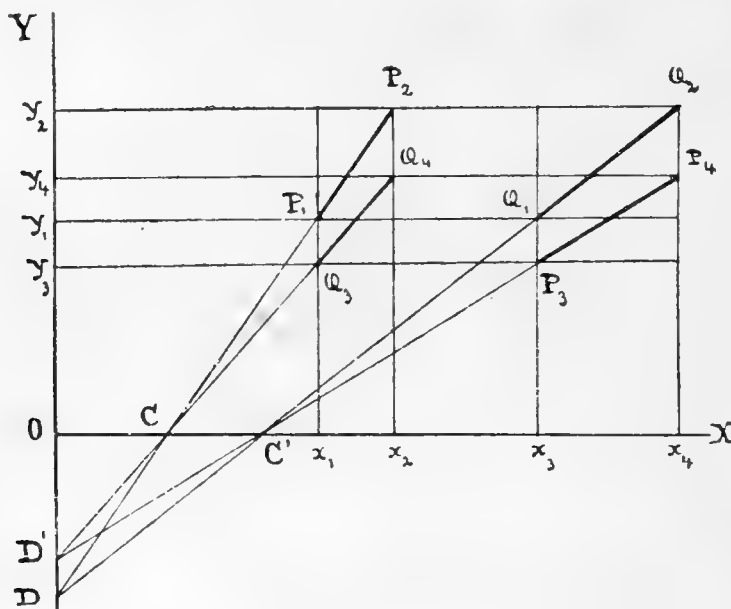


Fig. 11.

which two proportions are summarized in:

$$P_1 : P_2 = P_3 : P_4.$$

The rectangles having  $P_1 P_2$  and  $P_3 P_4$  as diagonals, are congruent now in a rational sense. With a view to the above mentioned proportions the rational sides are equal and likewise as immediate consequence, the rational areae:

$$\frac{x_2}{x_1}, \frac{y_2}{y_1} = \frac{x_4}{x_3}, \frac{y_4}{y_3}.$$

By means of proportional translation we can always construct

by way of points a figure which is rational congruent with a given figure. Rational congruence is of course originated by means of potential augmenting of the ratios. If in fig. 11 the ratio of the abscissae is equal to that of the ordinates we have ordinary congruence; the points  $C$  and  $D$  then coincide with  $O$ .

§ 30. In case two of the just mentioned four points coincide, the points are "corrational"; the middle point is then situated mean proportionally. A more general relation for corrational points is

$$P^a \times Q^b = R^{a+b} \quad \text{or} \quad (P:R)^a = (R:Q)^b;$$

$R$  divides the rational distance  $P, Q$  logarithmical proportionally according to:

$$\sqrt[a]{\frac{R}{Q}} = \sqrt[b]{\frac{P}{R}} = \sqrt[a+b]{\frac{P}{Q}}.$$

By drawing the root the logarithms of the rational weights ( $a$ ,  $b$  and  $a + b$ ) can be varied so that  $a + b = 1$ . In fig. 11 the points  $P$  form the vertices of a rational parallelogram of which  $P_0$  satisfying:

$$P_0^2 = P_1 \times P_4 = P_3 \times P_2$$

is the centre; this point is the geometrical mean of the diagonals. If now the point ratio is called the "freerational vector", then the rational distance  $P_1, P_2 = P_2^{LP_1}$  must be regarded as "bound rational vector" (§ 27).

In the field of difference a point ratio has no significance, the product of points only when the exponents are missing. It will therefore be right to furnish the rational product with a multiplicative sign. By ascending to the rootfield the mutual root of two points, having no importance for the field of ratio, will represent a free vector. The product of two free vectors is again a free vector; this can then be regarded as a resultant of the two. This is easy to see when we move one of the vectors until one end coincides with one of the ends of the other vector.

§ 31. It is easy to see the following theorems.

II. The product of point and free vector is a point.

III. The mutual power of a point with a free vector is a bound vector:

$$P_1, \frac{P_2}{P_1} = P_1, P_2 : P_1, P_1 = P_1, P_2.$$

That for three points of a rational holds simultaneously:

$$\frac{P_3}{P_2} = \frac{P_2}{P_1} \quad \text{and} \quad P_3, P_2 = P_2, P_1$$

can be seen by bringing the members of the first equation with  $P_2$  in mutual power; we then find:

$$P_3, P_2 = 1 : P_1, P_2 = P_2, P_1.$$

IV. The mutual power of two free vectors is called "bivector."

This is connected with the rational area of the rational triangle enclosed by the vectors made to coincide in a point, and the vector connecting the ends:

$$\frac{P_2}{P_1}, \frac{P_3}{P_1} = \sqrt{\left(P_1, \frac{P_2}{P_3}\right) \times \left(P_2, \frac{P_3}{P_1}\right) \times \left(P_3, \frac{P_1}{P_2}\right)}.$$

V. A bivector is represented by the product of 3 bound vectors. Simultaneously we find again for a rational triangle

$$\Delta = (P_1, P_2) \times (P_2, P_3) \times (P_3, P_1) \quad \text{and} \quad \frac{P_2}{P_1} \times \frac{P_3}{P_2} \times \frac{P_1}{P_3} = 1.$$

VI. A bivector is equal to the product of two equal, equidistant bound vectors with reciprocal values (fig. 10).

$$\frac{P_2}{P_1}, \frac{P_3}{P_1} = \left(\frac{P_2}{P_1}, P_3\right) : \left(\frac{P_2}{P_1}, P_1\right) = \left(\frac{P_4}{P_3}, P_3\right) \times (P_1, P_2) = (P_1, P_2) \times (P_3, P_4)^{-1}.$$

VII. The mutual power of point and bivector is a bound triangle; at the same time the mutual power of a free vector with a bound one

$$P_1, \left(\frac{P_2}{P_1}, \frac{P_3}{P_1}\right) = (P_1, P_2), \frac{P_3}{P_1} = P_1, P_2, P_3.$$

VIII. The product of a bound vector with a bivector is again a bound vector:

$$(P_1, P_2) \times \left(\frac{P_3}{P_1}, \frac{P_2}{P_1}\right) = P_3, P_4.$$

IX. The product of two bound vectors with the same origin is again a bound vector.

X. Each point in the field of ratio can be replaced by the product of three points, each provided with an exponent representing the logarithm of the weight. This can be seen in different ways:

$$P = E_1^{a_1} \times E_2^{a_2} \times E_3^{a_3} \quad ; \quad a_1 + a_2 + a_3 = 1.$$

We might replace  $e^a$  by  $g$ , we then find:

$$g_1 = (P_1, E_2, E_3) | (E_1, E_2, E_3) \text{ etc.}$$

The weights (having the character of numbers), are logarithmically proportional to the rational areae of the opposite triangles. If  $P$  is the centre of gravity of the fundamental triangle, then the weights are mutually equal to  $\frac{1}{3}e$ .

§ 32. We must then still mention the difference which must be made between the outer and the inner power of two rational vectors, of which the latter is always a scalar. It is natural to take in the

further considerations  $\bar{e}$  as base vector; for continuous change the ends form the logarithmic circle. If then still the mutually perpendicular vectors  $\bar{e}_x$  and  $\bar{e}_y$  are introduced we can write for a free vector:

$$\frac{P_2}{P_1} \left( = \frac{P}{1} \right) = \bar{\varrho} = (\varrho_1, \bar{e}_x) \times (\varrho_2, \bar{e}_y),$$

corresponding to the previously mentioned equation:

$$\frac{P_2}{P_1} = \frac{x_2}{x_1} \times \left( \frac{y_2}{y_1} \right)^i$$

For the outer power, which is, indeed, a bivector, holds:

$${}^2(\bar{e}_x) = {}^2(\bar{e}_y) = 1 \quad ; \quad (e_x, e_y) = (e_y, e_x)^{-1} (= e)$$

or reversely, according to the choice of the positive sense of revolution, which is evident from the determination of the multiplical:

$$(\bar{e}_x, \bar{e}_y) = \frac{e}{1} P e^{dLx} = [x]_1^e = e \quad ; \quad (\bar{e}_y, \bar{e}_x) = \frac{1}{e} P e^{dLy} = [y]_e^1 = \frac{1}{e}.$$

When introducing the rational angles we arrive for the outer power and the inner respectively at the following equations:

$$(\bar{\varrho}_1, \bar{\varrho}_2) = \varrho_1, \varrho_2, sr \frac{u_2}{u_1} \quad ; \quad [\bar{\varrho}_1, \bar{\varrho}_2] = \varrho_1, \varrho_2, cr \frac{u_2}{u_1}.$$

Of this important applications can be made.

§ 33. In the plane the mode of reckoning with complex powers is not inferior to the one with vectors. To determine the situation of a point in the field of ratio we can use:

$$xy^i = \varrho^{(-1) \frac{\varphi}{\pi}} = \varrho, \frac{Lu}{\pi} \left( \frac{1}{e} \right) = \varrho, e^{u, \sqrt{-1}}$$

from which ensues:

$$x = \varrho, cr u \quad ; \quad y = \varrho, sr u.$$

The multiplication of two directed areae (or vectors) mentioned in § 8 leads to the rational cosinus formula:

$$\varrho_0 = \sphericalangle \left[ {}^2(\varrho_1) \cdot {}^2(\varrho_2) \cdot \left( \varrho_1, \varrho_2, cr \frac{u_1}{u_2} \right)^2 \right];$$

the mutual power to the analogon of DE MOIVRE'S formula:

$$\bar{\varrho}_1, \bar{\varrho}_2 = \varrho_1, \varrho_2, e^{(u_1 u_2), \sqrt{-1}}.$$

From this can again be deduced

$${}^n(cr u \cdot sr^i u) = cr(u^n) \cdot sr^i(u^n),$$

besides

$${}^n(e^{u, \sqrt{-1}}) = e^{u^n, \sqrt{-1}},$$

which can again serve for the deduction of rational goniometric relations and for the development in series of product.

**Anatomy.** — „*Contribution to the knowledge of the development of the vertebral column of man*”. By Prof. Dr. E. W. ROSENBERG.  
(Communicated at the meeting of March 30, 1912).

The investigation, about which I wish to make a communication, was in the first place made by me with the intention, to test by new material my view regarding the existence of processes of transformation in the vertebral column of man, because this view, though it has been affirmed by several investigators, has been repeatedly contradicted, also of late years.

Furthermore I wished to make my investigation owing to a plan, communicated by me a long time ago, to utilize the work in the preparation-room for a purely scientific purpose<sup>1)</sup>.

In view of both intentions it was necessary to obtain a knowledge as complete and exact as possible, of the differences in form and composition, that the vertebral column of full-grown man can show, and moreover in such a way, that always the whole vertebral column and not only a part of it is examined. Neither was it allowed to make a choice among the objects that were at disposal, whereby preference was given to rare or more interesting observations; all the available vertebral columns, provided that they were complete, were to be used for the investigation. But on account of the anthropological side of the scientific work in the preparation-room, I had to put aside the vertebral columns of anonymous persons and of persons belonging to other nations than the Dutch.

Consequently my investigation regards the vertebral columns of born Dutchmen.

On account of the small number of corpses that were at my disposal at Utrecht, I was obliged to collect during a period of time, running from the autumn of 1888 to the end of 1899, in order to get 100 vertebral columns that satisfied the requirements.

In the period from 1900 till the present day a second hundred has not yet been obtained.

In the treatment of the vertebral columns I have not followed the usual method of preparation by which maceration is applied, because small parts are easily lost when is followed this method and because in adjusting again the bones of a vertebral column, isolated by maceration, arbitrariness and inaccuracy cannot be avoided.

<sup>1)</sup> E. ROSENBERG, Eine vergleichende Beurtheilung der verschiedenen Richtungen in der Anatomie des Menschen. Antrittsvorlesung, gehalten in Utrecht d. 28. Sept. 1888. Leipzig 1889, p. 43—47.

E. ROSENBERG, Ueber wissenschaftliche Verwerthung der Arbeit im Praeparirsaal. Morpholog. Jahrbuch, Bd. XXII, p. 561—589. 1895.

I have preserved the objects in alcohol, and prepared them myself with knife and pincette, by which operation the bones remained connected by natural ligaments. The preparations are placed in alcohol and a number of the drawings have been copied at an enlargement of  $\frac{1}{2}$  <sup>1)</sup>.

If one can agree to the view that transformation-processes take place in the vertebral column, the examined 100 vertebral columns can be divided, on account of certain peculiarities of these processes, into two groups.

One group contains 80 specimens, the other 20. These figures indicate already, that the first mentioned group is the more important one. This be therefore discussed first.

Not one of the 80 vertebral columns is perfectly identical with another.

Most points of difference are little deviations in form, which however morphologically are not without signification. If one leaves these aside, and pays only attention to differences that are so great, that they can influence the formula of the vertebral column, one sees, that in the group of 80 vertebral columns *ten different forms* are represented, which can be indicated by formulas. These are the formulas *I* *f* to *IIa* and *IIc* to *IIIb* of the subjoined list; vide page 82.

As an explanation of these formulas it be pointed out, that the vertebrae are indicated by figures, denoting their place in the column. The counting starts from the atlas as the first vertebra.

The vertebrae in different vertebral columns that are indicated by the same figure, are morphologically equivalent, because it has appeared, that in case of transformations of vertebral columns no vertebra falls out of the series, or is newly formed in the series between vertebrae, that exist already.

According to their form the vertebrae are taken in groups — the regions of the vertebral column — and the vertebrae in each region are indicated by letters corresponding with the names of the regions.

The vertebrae of the cervical region are indicated by *cv*. In the normal vertebral column this region contains the first vertebra up to the 7<sup>th</sup> included.

The vertebrae of the dorsal region are indicated by *d*. There are 12, consequently the 8<sup>th</sup> up to the 19<sup>th</sup> included. They are characterized by the fact, that each vertebra is provided with one pair of ribs movably united to it.

<sup>1)</sup> These drawings were demonstrated at the meeting; they will be published on another occasion.

The vertebrae of the lumbal region are indicated by *l*. There are 5 of them, consequently the 20<sup>th</sup> up to the 24<sup>th</sup> vertebra included. Their peculiarity is, that reduced ribs are completely coalesced with the transverse processes, consequently projecting parts are formed which are called processus laterales.

The vertebrae of the sacral region are indicated by *s*. There are 5 of them, consequently the 25<sup>th</sup> up to the 29<sup>th</sup> vertebra inclusive; they have processus laterales of the same morphological value as the lumbal vertebrae. But the sacral vertebrae have these processus fused together at the lateral extremities on either side of the body. This occasions the formation of the pars lateralis sacri, with which the girdle of the lower extremity articulates. The bodies of these vertebrae fuse likewise together at the formation of the os sacrum.

The vertebrae of the caudal region are indicated by *cd*. There

LIST OF FORMULAS OF THE VERTEBRAL COLUMN.

<i>IV</i>	1.—7. <i>cv</i>	8.—18. <i>d</i>	19.—23. <i>l</i>	24.—28. <i>s</i>	29.—32. <i>cd</i>
<i>III<sub>f</sub></i>	1.—7. <i>cv</i>	8.—18. <i>d</i>	19.—23. <i>l</i>	24. 28. <i>s</i>	29.—33. <i>cd</i> )
<i>III<sub>e</sub></i>	1.—7. <i>cv</i>	8. 18. <i>d</i>	19.—23. <i>l</i>	24.—28. <i>s</i>	29. <i>scd</i> 30.—33. <i>cd</i> )
<i>III<sub>d</sub></i>	1.—7. <i>cv</i>	8.—18. <i>d</i>	19.—23. <i>l</i>	24.—29. <i>s</i>	30.—33. <i>cd</i> )
<i>III<sub>c</sub></i>	1.—7. <i>cv</i>	8.—18. <i>d</i>	19. <i>dl</i> 20.—23. <i>l</i>	24.—29. <i>s</i>	30.—33. <i>cd</i> )
<i>III<sub>b</sub></i>	1.—7. <i>cv</i>	8.—19. <i>d</i>	20.—23. <i>l</i>	24.—29. <i>s</i>	30.—33. <i>cd</i>
<i>III<sub>a</sub></i>	1.—7. <i>cv</i>	8.—19. <i>d</i>	20.—23. <i>l</i>	24. <i>ls</i> 25.—29. <i>s</i>	30.—33. <i>cd</i>
<i>III</i>	1.—7. <i>cv</i>	8.—19. <i>d</i>	20.—24. <i>l</i>	25.—29. <i>s</i>	30.—33. <i>cd</i>
<i>II<sub>f</sub></i>	1.—7. <i>cv</i>	8.—19. <i>d</i>	20.—24. <i>l</i>	25.—29. <i>s</i>	30.—34. <i>cd</i>
<i>II<sub>e</sub></i>	1.—7. <i>cv</i>	8.—19. <i>d</i>	20.—24. <i>l</i>	25.—29. <i>s</i>	30. <i>scd</i> 31.—34. <i>cd</i>
<i>II<sub>d</sub></i>	1.—7. <i>cv</i>	8.—19. <i>d</i>	20.—24. <i>l</i>	25.—30. <i>s</i>	31.—34. <i>cd</i>
<i>II<sub>c</sub></i>	1.—7. <i>cv</i>	8.—19. <i>d</i>	20. <i>dl</i> 21.—24. <i>l</i>	25.—30. <i>s</i>	31.—34. <i>cd</i>
<i>II<sub>b</sub></i>	1.—7. <i>cv</i>	8.—20. <i>d</i>	21.—24. <i>l</i>	25.—30. <i>s</i>	31.—34. <i>cd</i>
<i>II<sub>a</sub></i>	1.—7. <i>cv</i>	8.—20. <i>d</i>	21.—24. <i>l</i>	25. <i>ls</i> 26. 30. <i>s</i>	31.—34. <i>cd</i>
<i>II</i>	1.—7. <i>cv</i>	8.—20. <i>d</i>	21.—25. <i>l</i>	26.—30. <i>s</i>	31.—34. <i>cd</i>
<i>I<sub>f</sub></i>	1.—7. <i>cv</i>	8.—20. <i>d</i>	21.—25. <i>l</i>	26.—30. <i>s</i>	31.—35. <i>cd</i>
<i>I<sub>e</sub></i>	1.—7. <i>cv</i>	8.—20. <i>d</i>	21.—25. <i>l</i>	26.—30. <i>s</i>	31. <i>scd</i> 32.—35. <i>cd</i> )
<i>I<sub>d</sub></i>	1.—7. <i>cv</i>	8.—20. <i>d</i>	21. 25. <i>l</i>	26.—31. <i>s</i>	32.—35. <i>cd</i> )
<i>I<sub>c</sub></i>	1.—7. <i>cv</i>	8.—20. <i>d</i>	21. <i>dl</i> 22. 25. <i>l</i>	26.—31. <i>s</i>	32.—35. <i>cd</i> )
<i>I<sub>b</sub></i>	1.—7. <i>cv</i>	8.—21. <i>d</i>	22.—25. <i>l</i>	26.—31. <i>s</i>	32.—35. <i>cd</i> )
<i>I<sub>a</sub></i>	1.—7. <i>cv</i>	8.—21. <i>d</i>	22.—25. <i>l</i>	26. <i>ls</i> 27.—31. <i>s</i>	32.—35. <i>cd</i> )
<i>I</i>	1.—7. <i>cv</i>	8.—21. <i>d</i>	22.—26. <i>l</i>	27.—31. <i>s</i>	32.—35. <i>cd</i> )



are 4 of them, consequently the 30<sup>th</sup> up to the 33<sup>rd</sup> included. They are characterized by a very reduced form.

On the boundaries between the regions vertebrae may be found showing the peculiarities of vertebrae of two regions.

Between the dorsal region and the lumbal region a vertebra may occur, bearing on one side of the body a small rib and on the other a processus lateralis. Such a vertebra is called dorsolumbal vertebra and indicated in the formula by *dl*.

Between the last typical lumbal vertebra and the first sacral vertebra a vertebra may exist, touching either on the right or the left with its thickened processus lateralis the pars lateralis of the sacrum or uniting with it. This is a lumbosacral vertebra indicated by *ls*.

Between the sacrum and the first caudal vertebra a vertebra may exist, not showing on one or on either side the connection with the pars lateralis, yet being united with the body of the preceding vertebra. This intermediate form is called a sacrocaudal vertebra and is indicated in the formula by *scd*.

Now the ten forms of the vertebral column that are represented in the group of 80 specimens can be regarded more closely.

One of these forms is the "normal vertebral column"; it has the formula *III*.

The nine others differ among each other and with regard to the normal vertebral column especially in that part that contains the distal part of the dorsal region with the sternum and the arcus costarum and further all following regions in a distal direction.

In the cervical region likewise differences are to be detected, they are however not so great, as to influence the formula. Though these differences are by no means without signification, I shall not discuss the cervical region, in order not to take up too much time, and I shall likewise pass over in silence the arcus costarum and confine myself to that part of the vertebral column that begins at the 18<sup>th</sup> vertebra; this is in *all* specimens the 11<sup>th</sup> dorsal vertebra.

By many authors the different forms of the vertebral column occurring beside the so called normal vertebral column, are in a certain respect contrasted with the latter.

They are looked upon as variations or varieties or fluctuating modifications that are a result of the variability of the organism. These deviating forms are consequently regarded as oscillations, surrounding a constant form, representing the central point — i. e. the normal vertebral column — either at equal distances or in an irregular manner.

In my opinion this view which of late years has still been defended e.g. by DWIGHT<sup>1)</sup>, BARDEEN<sup>2)</sup>, FISCHEL<sup>3)</sup> is not very satisfying.

In opposition to this view I wish to hold another, at which one arrives when making use of the notions of comparative anatomy and certain results of embryology.

If we cast a look at the above ten formulas, we are struck by the difference in the number of vertebrae as regards both the whole vertebral column and the praesacral and the dorsal part.

In a vertebral column of the formula *I f* 35 vertebrae are extant in toto, among which are 25 praesacral and 13 dorsal ones.

On the contrary we find in a vertebral column of the formula *III b* in toto 33 vertebrae, 23 of which are praesacral and 12 dorsal.

Now comparative anatomy teaches, that if we leave out of consideration the stages of the vertebral column, which form the beginning of the phylogenesis of this organ, a comparatively greater number of vertebrae characterizes a more primitive state. Consequently a vertebral column of the formula *I f* is more primitive than a column answering to the formula *III b*.

And as embryological investigation<sup>4)</sup> has shown us, it is true, that a lumbal vertebra can be transformed into a sacral vertebra, but the opposite process has not been demonstrated, and further, because the study of the development of the vertebral column of man has proved, that a little rib can fuse with the transverse process of a vertebra, and consequently can contribute to the formation of a processus lateralis, but never has anything been observed, which

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<sup>1)</sup> TH. DWIGHT, Description of the Human Spines showing Numerical Variation in the Warren Museum of the Harvard Medical School. Memoirs of the Boston Society of Natural History vol 5. N. 7. 1901 p. 237—312.

TH. DWIGHT, Numerical Variation in the Human Spine, with a Statement concerning Priority. Anatom. Anzeiger. Bd. XXVIII p. 33—40; 96—102. 1906.

<sup>2)</sup> CH. R. BARDEEN. Numerical vertebral Variation in the human Adult and Embryo. Anatom. Anzeiger. Bd. XXV 1904 p. 497—519.

CH. R. BARDEEN, Studies of the development of the human skeleton. With 13 pl. American Journ of Anatomy. Vol IV N. 3 p. 265—302 Pl. 1—XIII. 1905.

Compare likewise the chapter written by BARDEEN: "Die Entwicklung des Skeletts und des Bindegewebes" in the Handbuch der Entwicklungsgeschichte des Menschen, herausgegeben von F. KEIBEL und F. P. MALL. Bd. I Leipzig 1910 p. 326, p. 360—362.

<sup>3)</sup> A. FISCHEL, Untersuchungen über die Wirbelsäule und den Brustkorb des Menschen. Anatom. Hefte. Herausgegeben von F. MERKEL und R. BONNET. Bd. XXXI p. 459—588. M. Tf. 51—60. 1906.

<sup>4)</sup> Regarding the observations to be taken into consideration here, vide: E. ROSENBERG, Bemerkungen über den Modus des Zustandekommens der Regionen an der Wirbelsäule des Menschen. Morpholog. Jahrbuch Bd. XXXVI H. 4 p. 609—659. 1907.

might prove that a vertebra without any ribs is being provided with the latter in the course of ontogenesis, so, in view of these facts, a vertebral column of the formula *If* is more primitive than others that have fewer praesacral vertebrae and fewer dorsal vertebrae.

Consequently we may take the vertebral column *If* as our starting-point when considering the above mentioned 10 formulas.

If now in a vertebral column of this form the 35<sup>th</sup> vertebra is completely reduced, the result is a vertebral column of the formula *II* which, otherwise, with regard to the composition of the regions, corresponds with the vertebral column *If*. When comparing the illustrations, however, one can see that in the vertebral column *II* the 13<sup>th</sup> pair of ribs consists of smaller bones and that the processus lateralis of the 25<sup>th</sup> vertebra are thicker, and that they are likewise nearer to the pars lateralis sacri.

These are but little differences of form, but they are forerunners of greater ones.

This is already seen in the specimen, representing the formula *IIa*. Here the 25<sup>th</sup> vertebra is a lumbosacral vertebra.

This state of things becomes intelligible, when we consider, that the sacrum is formed, because the girdle of the lower extremities rests on the vertebral column and that therefore a number of vertebrae fuse. Further one must pay attention to the fact that the girdle of the extremity, (being the ossa coxae), is not connected with the whole extent of the pars lateralis but only with a proximal part of it. This fact shows, that the pars lateralis did not come into existence at once in its whole extent, but developed successively, and the part of the pars lateralis that in a given vertebral column is in connection with the ossa coxae, has been formed later or is younger, than the part lying more distally; this part was previously connected with these bones, but lost this connection because the girdle of the extremity was displaced in a proximal direction.

At first sight this view seems to be a very hypothetical one, but it can be proved.

Let us suppose that the girdle of the extremity in a vertebral column of the formula *II* be removed only a little in a proximal direction, then the 25<sup>th</sup> vertebra is more strongly influenced by the ossa coxae. The more intense functional requirements cause a stronger development of the processus laterales, which can soon increase so much, that on one side of the body the thickened processus lateralis touches the pars lateralis and unites with it. In this way the 25<sup>th</sup> vertebra can become a lumbosacral vertebra.

This has been the case with the vertebral column *IIa*, where the

thickened processus lateralis is already connected with the right hand os coxae. Moreover the vertebral column *IIa* shows, that the 13<sup>th</sup> pair of ribs is still more reduced; they are still only little pieces of bone which are however movably united with the processus transversi.

In the vertebral column *IIc* we see, that the 25<sup>th</sup> vertebra is on both sides of the body attached to the pars lateralis and has consequently become the first sacral vertebra. And as in the distal part of the vertebral column no important modification has taken place, we find now a sacrum consisting of six vertebrae. At the same time at the 20<sup>th</sup> vertebra on one side the rib has fused with the vertebra, on the other side the rib has remained extant. Consequently the vertebra has become a dorsolumbal vertebra. Now there are only 4 lumbar vertebrae extant, as is likewise the case in *IIa*.

The next form, *IId*, develops, when, on both sides of the body, at the 20<sup>th</sup> vertebra rudimentary ribs have disappeared as independent parts. This vertebra has now become the first lumbar vertebra; there are again 5 lumbar vertebrae, and in the praesacral part the arrangement has taken place that characterizes the normal vertebral column. In the sacrum there are however still 6 vertebrae to be found.

In vertebral columns of the form *IIE* the praesacral part is conform to that of *IId*. At the distal extremity of the sacrum, however, now peculiarities can be observed, showing that the 30<sup>th</sup> vertebra is loosened from the sacrum. In the specimen represented the pars lateralis is interrupted between the 29<sup>th</sup> and the 30<sup>th</sup> vertebra on the right side of the body, in other specimens this is the case on the other side or on both sides; in these cases the 30<sup>th</sup> vertebra is only connected with the sacrum by its body. In all these cases the 30<sup>th</sup> vertebra has become a sacrocaudal vertebra.

If now the 30<sup>th</sup> vertebra is separated from the sacrum also with regard to the body, then a vertebral column is formed that is indicated by the formula *IIf*. This has a sacrum composed again of 5 vertebrae. But now of course 5 caudal vertebrae are extant, because, as already in the form *II*, the 34<sup>th</sup> vertebra still closes the series.

The consequence of a complete reduction of the 34<sup>th</sup> vertebra is a vertebral column of the normal form; the formula is indicated by *III*, which has been done for good reasons.

If we compare namely the formula *III* with the formula *II*, it appears, that the dorsolumbal boundary, the lumbosacral boundary, and the sacrocaudal boundary have all three been displaced one vertebra in a proximal direction, and that at the end of the vertebral column one vertebra has disappeared.

It is not for the first time that in the so-called normal vertebral

column displacement of the boundaries of the above-mentioned regions has caused the existence of 5 lumbal, 5 sacral and 4 caudal vertebrae but, as can be shown with great probability, it is for the third time in the course of the phylogenetical development of the human vertebral column. In vertebral columns of the formula *II* it is the second time that such an arrangement has taken place. This follows from observations in a vertebral column, in which, in so far as at present the history of the human vertebral column is known to us, for the first time groups of 5 lumbal, 5 sacral, and 4 caudal vertebrae have appeared. These observations will be cited afterwards.

This induced me, to divide the formulas into groups indicated by figures. This facilitates the general survey and gives, as will afterwards prove, still another advantage.

Now we have still to look at the formulas *IIIa* and *IIIb*.

From the formula *IIIa* it appears, that now the 24<sup>th</sup> vertebra has obtained a lumbrosacral form. And the illustration shows, that the 12<sup>th</sup> pair of ribs is a little shorter than in the vertebral column *III*. This points to a beginning reduction of the mentioned pair of ribs.

The form *IIIa* is evidently analogous to the form *IIa* and, like this, the vertebral column *IIIa* shows that a removal in a proximal direction of the girdle of the extremity occasions a modification in the composition of the regions, and that the formation of a lumbosacral vertebra is again the first act in the progress of the transformation-process.

The formula *IIIb* and the sketched specimen represent a further advancement of the process. The 24<sup>th</sup> vertebra has now become the first sacral vertebra, we can, however, easily conclude from the form of this vertebra that from a lumbal vertebra it has been transformed to a sacral vertebra. Of course there are now again 6 sacral vertebrae, as in the case of the sacra of *IIc* and *IId*. In vertebral columns of the form *IIIb* we see distinctly, that the 12<sup>th</sup> pair of ribs has been reduced still more; in one of the specimens it is almost as little as the 13<sup>th</sup> pair of the vertebral column *If*.

If we take now a survey of the ten forms of the vertebral column just discussed, we may, in my opinion, assert that the view as if nine of these forms should only be insignificant oscillations of the organisation, surrounding as variations or varieties a constant form — the normal vertebral column — in an irregular way, does not explain the stated facts in a satisfactory manner. On the contrary these facts confirm the view I have defended long since.

It is so clear, that the discussed forms of the vertebral column are parts or links of a morphological succession or chain (morpho-

logische Reihe) that when describing the forms I could hardly help assigning a share in this description to the part of the phylogenetical development that is to be inferred from this chain.

Because the separate forms can be joined together freely and in a definite direction to a morphological succession, it is clear, that there is no contrast between a normal form of the vertebral column and varieties. All these ten forms are principally of equal value; they are representatives of stages of development, following each other successively.

The so-called normal vertebral column is the form that is at present numerically predominant.

Vertebral columns representing the formulas *I*f to *III*f are retarded forms that have stopped at different stages, preceding stage *III*.

And of course forms with a formula as *III*a or *III*b must be regarded as forms of a higher development than the normal vertebral column, having the value of future forms.

It seems to me that this view is more satisfying than the other and at the same time admits of the possibility of a certain application, which the other does not allow.

The application, I mean, becomes evident, when we pay attention to the fact, that the stages of development hitherto stated distinguish themselves, with only one exception, by only one phenomenon of transformation that can be indicated in the formula. The distance between each other of these stages of development is consequently in a morphological sense the same.

This is the case with the stages *I*f to *II*a and *II*c to *III*b.

If however we compare the forms *II*a and *II*c, we see that in the latter two phenomena of transformation are present, namely a transformation of the 25<sup>th</sup> vertebra into a first sacral vertebra, and of the 20<sup>th</sup> vertebra into a dorsolumbal vertebra.

The distance between these two forms is consequently greater than between the others. This suggests the supposition, that between the stages *II*a and *II*c a stage might exist, characterized by the fact that the 25<sup>th</sup> vertebra has already become a sacral vertebra, whilst the 20<sup>th</sup> vertebra has still remained the last dorsal vertebra.

To this answers a formula *II*b, which I have inserted into the series provisionally as an hypothetical one. I have in vain looked for such a form among the 100 vertebral columns under consideration. When studying the specimens, which I am collecting for the second hundred, I have however found the designated form of the vertebral column and even three times.

The formula *II*b is therefore no longer an hypothetical one.

The confirmation of one deduction of such a nature causes us to construe others from the observations we have made.

Now that the series of formulas from *If* to *IIIb* shows no longer an hiatus, it is possible, proceeding from the extremities of the series, to follow to a certain degree the process of transformation forward and backward, and to indicate the stages by hypothetical formulas.

The formula *IIIb* is analogical to the formula *IIb*, and in analogy to the formula *IIc* we can add to the formula *IIIb* a formula *IIIc*, indicating that the last dorsal vertebra of *IIIb*, the 19<sup>th</sup> of the series, has become a dorsolumbal vertebra.

When, by reduction of the rib still existing on one side of the 19<sup>th</sup> vertebra, this becomes a first lumbar vertebra, then we have the form *IIId*, in which, as in *IIIb* and *IIIc*, a sacrum consisting of 6 vertebrae must be extant.

Now we can imagine, that the 29<sup>th</sup> vertebra becomes a sacrocaudal vertebra and thus the formula *IIIc* is given.

And when now this 29<sup>th</sup> vertebra has passed into the series of the caudal vertebrae, the result is a vertebral column having the formula *IIIf*, which, as the formulas *IIf* and *If*, is characterized by the existence of 5 caudal vertebrae, the last, however, is now the 33<sup>rd</sup> of the series.

The reduction of this 33<sup>rd</sup> vertebra gives a formula *IV*, an analogon to formula *III*, and now once more the dorsolumbal boundary, the lumbosacral boundary and the sacrocaudal boundary have been displaced one vertebra in a proximal direction, and at the distal extremity one vertebra has disappeared. Consequently for the fourth time successive groups of 5 lumbar, 5 sacral, and 4 caudal vertebrae would be extant.

I have not hesitated to mention these conclusions, because formula *IV* may indeed not be considered to be a hypothetical one. A vertebral column of this composition has been described more particularly by TENCHINI<sup>1)</sup> in Parma, who however adheres to the then already refuted doctrine of excalation, and supposes, that the 12<sup>th</sup> dorsal vertebra with its ribs is entirely missing. A similar vertebral column has also been observed and briefly described by BIANCHI<sup>2)</sup> in Siena.

Whether this process will continue further, cannot be said with certainty; it might be possible.

1) L. TENCHINI, Mancanza della dodicesima vertebra dorsale e delle due ultime coste etc. L'Ateneo Medico Parmense, Anno 1. Fasc. 2 p. 97—132. Parma 1887.

2) S. BIANCHI, Sulla frequenza delle anomalie numeriche vertebrali nello scheletro dei normali e degli alienati. Atti della R. Accad. dei Fisiocritici in Siena. Ser. IV, vol VII Fasc. 1—2. p. 29, osservazione V. Siena 1895.

Now, proceeding from the actually observed form *If*, one might cast a look into a comparatively ancient period of the history of the vertebral column.

If in analogy of the formulas *IIIf* to *II* one were to construe succeeding formulas to the formula *If*, the first in succession would be a formula, denoting the 31<sup>st</sup> vertebra as a sacrocaudal vertebra: *Ie*.

The latter must be preceded by a form of the vertebral column in which the 31<sup>st</sup> vertebra is the last and moreover the sixth sacral vertebra: *Id*. Here the 21<sup>st</sup> vertebra must be the first lumbal vertebra as in the formulas *IIc* to *Ie*.

Inasmuch as now a first lumbal vertebra is developed from a last dorsal vertebra, after it has passed through the stage of a dorsolumbal vertebra, the next following more primitive form must possess the 21<sup>th</sup> vertebra as dorsolumbal vertebra, as is indicated in the formula *Ic*.

And this must have been developed from a form in which the 21<sup>st</sup> vertebra is the last and moreover the 14<sup>th</sup> dorsal vertebra, which characterizes the formula *Ib*. In this formula the 26<sup>th</sup> vertebra is the first of a sacrum, consisting of 6 vertebrae. A first sacral vertebra, however, develops from a last lumbal vertebra, after it has been lumbosacral vertebra.

Consequently we can imagine a formula, showing the 26<sup>th</sup> vertebra as lumbosacral vertebra, in which at the same time 14 dorsal vertebrae and 4 lumbal vertebrae are extant, besides a sacrum, consisting of five vertebrae. This is indicated in the formula *Ia*.

And if now we go one step more backward, then it must be possible to find a vertebral column in which the 26<sup>th</sup> vertebra is the last and moreover the 5<sup>th</sup> lumbal vertebra, then a sacrum of 5 vertebrae must follow and 4 caudal vertebrae must succeed to this, the last of which is the 35<sup>th</sup> vertebra of the series. This gives the formula *I*.

With regard to the formulas *Ie* to *Ia* I must admit, that they are purely hypothetical; with regard to formula *I*, however, I should wish to cite an observation, answering almost entirely to this formula.

First I must, however, briefly fix the attention to a peculiarity, occurring in vertebral columns standing on the ten stages mentioned.

If a special stage is represented by more than one specimen we see in these specimens differences that have a morphological signification.

As an example I wish to cite the stage *IIIa*, which is represented by three vertebral columns.

One glance at the illustrations is sufficient to see that these three



specimens form a morphological progression, demonstrating a beginning of the reduction of the 12<sup>th</sup> pair of ribs.

At the same time it is very clear that these three specimens cannot be directly derived the one from the other, that consequently they do not form what might be called a descensional succession.

This shows the 24<sup>th</sup> vertebra. In specimen 1 the contact with the sacrum has been formed on the *right* side of the body, in the two other specimens on the *left* side. These three specimens consequently belong at least to two successions that have diverged, be it only in a slight degree.

And if in the specimens 2 and 3 we carefully examine the pars lateralis, then it appears from observations, which we cannot enter into particulars upon here, that the specimen 3 which, with regard to the twelfth pair of ribs, is higher developed than the specimen 2, is, with regard to the facies auricularis, more primitive than the specimen 2. Thus, likewise between these two specimens, there exists a slight divergence of development. All three specimens are consequently the extremities of three independent progressions of development, though they may be only very short.

As a second and last example the two specimens representing the stage *IIIb* may serve.

We see that the reduction of the 12<sup>th</sup> pair of ribs has reached a higher degree; in the specimen 2 these ribs are already so little that they look much like much reduced 13<sup>th</sup> ribs. Together with the specimens of the stage *IIIa* these two specimens exhibit, in the most convincing manner, the gradual reduction of the 12<sup>th</sup> pair of ribs.

The 24<sup>th</sup> vertebra is in the stage *IIIb* first sacral vertebra, and it is obvious that, in specimen 1, it is transformed in a slighter degree than in specimen 2.

With regard to these points (I leave other points out of discussion) specimen 2 is doubtless the higher developed one. That this specimen does not after all directly continue the line of development of specimen 1, but deviates from it divergently, appears from the position of the facies auricularis, which in specimen 2 is a less transformed one than in specimen 1. This is likewise seen, when considering the 30<sup>th</sup> vertebra. In specimen 2 this vertebra has still cornua coccygea, whereas these have already almost completely disappeared in specimen 1. This points likewise to divergent development.

*This divergency of development is shown by all specimens belonging to any stage.* It is however so slight that the specimens remain unmistakably within the boundaries of the separate stages.

It is however of importance to ascertain this divergency, because

it enables us to interpret the vertebral columns in the second, smaller group.

One need only suppose, that the divergency of the direction of development increases more or less, then forms must originate that do no longer fit in the frame of the separate stages, but are connected with every stage as *accessory forms*, as they might be called.

These forms remain by local, relative retardation or by local acceleration of the transformation, either below the stage, to which they belong, or they are a little more developed. But always they diverge from the direction that leads from one special stage to the other, and thereby they form, as it were, side-branches, which are however very short, because the several accessory forms are, as a rule, only represented by one single specimen.

The second group contains 20 vertebral columns, and these represent 17 different forms that can be denoted by formulas.

Only as one single example I wish to cite an accessory form, belonging to stage *II*. In this stage the 20<sup>th</sup> vertebra is the 13<sup>th</sup> dorsal vertebra; if this vertebra through comparatively too rapid transformation becomes a first lumbal vertebra, whilst the other parts of the vertebral column remain unaltered, then a vertebral column has been formed with 6 lumbal vertebrae. And we see that this column has not followed the line of development leading to stage *IIa*, because to this stage only 4 lumbal vertebrae belong. It has followed a side-path that leads away from the main-route and soon ends.

Let me mention a second example.

In the list of formulas stage *IIIb* is followed by a hypothetical stage *IIIc*, in which the 19<sup>th</sup> vertebra is a dorsolumbal vertebra. I have now found a vertebral column, belonging to the second group, in which the 19<sup>th</sup> vertebra has this form. To the left exists a processus lateralis and to the right a rudimentary 12<sup>th</sup> rib, which is about to fuse with the vertebra.

Further we find 4 lumbal vertebrae and a sacrum, consisting of 6 vertebrae, the 24<sup>th</sup> to the 29<sup>th</sup>, as must be the case in a stage *IIIc*. In so far everything agrees with what is indicated in the hypothetical formula. But the vertebral column I am dealing with, has only 3 caudal vertebrae and not 4, as the formula requires, the 32<sup>nd</sup> vertebra is the last.

Consequently I cannot regard this vertebral column as a representative of a stage *IIIc*; but it may be conceived as an accessory form to such a stage. By acceleration of the transformation at the distal end the 33<sup>rd</sup> vertebra has been reduced comparatively too early.

It seems to me that this observation makes it very probable that

it will be possible, to find the stage *IIIc*, which for the present is still hypothetical.

Principally in the same way the probability of the existence of the most primitive stage *I* can be shown.

This appears from observations I was allowed to make on a vertebral column in the anatomical institute of Leiden.<sup>1)</sup>

On account of the existence of articular planes on the 20<sup>th</sup> and the 21<sup>st</sup> vertebra it is certain that these vertebrae were provided with movable ribs that were missing in the preparation.

So here 14 dorsal vertebrae are to be found as formula *I* requires. Further we see 5 lumbal vertebrae, the 26<sup>th</sup> vertebra is the last lumbal one, then follows a sacrum, consisting of the 27<sup>th</sup> to the 31<sup>st</sup> vertebra, as the formula indicates. The caudal vertebrae of the preparation are defective, so that we cannot know whether the 35<sup>th</sup> vertebra was the last. The 32<sup>nd</sup> and the 33<sup>rd</sup> vertebrae are extant in the preparation, they have however a sacrocaudal form.

Consequently this vertebral column does not answer entirely to formula *I*, it is a little more primitive and may be regarded as an accessory form to a stage *I*.

The examples cited show that the accessory forms can likewise be explained, if we admit the view, that the various forms are not irregular varieties, but the consequences of special processes of development.

Having this view, we need no longer explain the existence of the various forms by the so called variability. This does indeed not give an explanation at all, neither does it make us understand that the great majority of the vertebral columns forms a morphological progression.

The observations I have made, become however intelligible, if we consider that when a species, consisting of many individuals, is in a state of phylogenetical development, it would be highly improbable, that all the individuals should be transformed with exactly the same rapidity.

If there is, however, a difference of rapidity or intensity of the transformation, then it is evident, that, at a given period, in individuals living at the same time, very different stages of the process of development of the whole species will be represented by groups of the individuals.

And this is what we have seen.

At the same time it is clear now, why the great majority of the

<sup>1</sup> E. ROSENBERG. Ueber eine primitive Form der Wirbelsäule des Menschen Morphol. Jahrbuch Bd XXVII, H. 1. p. 1—118, Tf. I—V. 1899.

individuals form a continuous progression of stages of development.

If we survey the whole progression, we can observe that the difference, existing between the most primitive stage and the highest, is greater than the differences in the composition of the vertebral columns not only in some species, but even in several genera of Primates.

Consequently it is not an unimportant part of the history of the human vertebral column that the formulas allow us to survey.

*Three* dorsal vertebrae have successively become proximal lumbal vertebrae, *three* distal lumbal vertebrae have the one after the other been lodged in the proximal part of the sacrum, and from the distal extremity of it gradually *three* vertebrae have passed into the caudal region, which has lost *three* vertebrae at the extremity.

The diminution of the number of praesacral vertebrae does, however, not necessarily involve a shortening of the trunk; by measurements we can come to the conclusion, that in the higher stages the bodies of the vertebrae become higher and this occasions a compensation.

In the sternum and the arcus costarum, too, analogous modifications take place.

All these observations justify the notion, that in the region of the trunk an important transformation is working; the processes in the vertebral column can certainly not take place, if the parts of the body, surrounding this extensive organ, do not participate in the transformation.

The knowledge of these processes must consequently exercise an influence on the descriptions which systematical and topographical anatomy give of the composition of the trunk. Both branches of science pay too little attention to the transformation of the organism.

I cannot enter into further details on this subject now; in conclusion I wish only to point out in a few words the importance of the series of formulas with regard to anthropology.

This becomes apparent when we consider, how the vertebral columns are arranged by the series of the stages.

The result appears from a graphical representation <sup>1)</sup>.

On horizontal lines, answering to the stages, the specimens belonging to each stage are indicated by dots.

At the end of each line the accessory forms are indicated by marks, placed either a little lower or a little higher, further is denoted, what characterizes each accessory form.

The rows of the representatives of each stage have been placed

<sup>1)</sup> This will be published in another communication.

symmetrically in relation to a line, indicating the route or course that is followed by the transformation of the species. If we consider this representation, it is in the first place remarkable that the so-called normal vertebral column has not the absolute majority, but only a relative one. There are in the stage *III* 26 vertebral columns.

Further the attention is drawn by the fact that the stages *IIf* and *III* contain a rather great number of specimens.

In the stage *IIf* the 30<sup>th</sup> vertebra is a sacrocaudal vertebra. The loosening of this vertebra from the sacrum is morphologically a complicated process; it is therefore clear that it is not so soon finished, and that consequently a rather great number of individuals are at the same time in stage *IIf*. There are 23 of them.

In stage *III* 5 caudal vertebrae are extant, the last is the 34<sup>th</sup> vertebra. This must be reduced, then the stage *III* is attained. The reduction of this vertebra is morphologically a comparatively simple process, consequently there are fewer specimens found in this stage than in stage *IIf*. This reduction, however, is physiologically of little importance; this may be a reason of retardation of the process, so that after all as many as 14 individuals have stopped in this stage.

It stands to reason that the more primitive and the most modified forms are found only in small numbers in the relative stages.

As the series of the formulas allows of an arrangement of the examined vertebral columns, this series gets the value of a *scale* or *standard* by which we can ascertain the degree of development, reached by the examined organ for every group of men that can anthropologically be distinguished.

It is true the number of 100 vertebral columns is not sufficient to pronounce a decisive opinion in an anthropological regard.

But in a methodological regard the result we have obtained is, in my opinion, sufficient to confirm the conviction, that, by this method, when many individuals are examined, it is possible to fix for every nation the degree of development, attained with regard to the organ examined or to other organs, provided that for each a series of stages be established.

So I am of opinion that it would be worth while applying this method of investigation to races of men that in anthropological regard stand widely apart from each other.

This might be done, if in preparation-rooms of various countries, provided with the required number of corpses, the same investigations were made.

It is very likely that rather different arrangements of individuals by the scale of the formulas would be found, and that it would

be possible to characterize anthropologically the different races of men by indicating the differences in the character and the intensity of the processes of transformation.

And if the vertebral column should be chosen for such an investigation, an opinion about the degree of organisation attained would certainly not rest on too narrow a basis, as the vertebral column is in contact with many organs that surround it, and actively or passively participate in its transformation.

**Physics.** — “*On vapour-pressure lines of binary systems with widely divergent values of the vapour-pressures of the components.*” (In connection with experiments of Mr. KATZ). By Prof. PH. KOHNSTAMM. (Communicated by Prof. VAN DER WAALS).

§ 1. *General character of the vapour-pressure lines derived from the differential quotients.* The theory of the  $p,x$ -lines of binary mixtures was developed by VAN DER WAALS in Verslagen Kon. Ak. v. Wet. (3) 8 p. 409 and These Proc. III p. 163 (See also Cont. II p. 120 et seq.) on the supposition that the quantity  $\mu'_{x_1}$  occurring there may

be represented by  $-\frac{d\frac{a_x}{b_x}}{dx}$ , and so is only dependent on the critical temperature of the mixture taken as homogeneous. VAN DER WAALS showed later on that a further approximation may be obtained by the introduction of the quantity  $p_c$ , the vapour-pressure of the mixture taken as homogeneous. Then:

$$\mu'_{x_1} = \frac{dlp_c}{dx}$$

while :

$$-l\frac{p_c}{p_k} = f\left(\frac{T_k}{T} - 1\right).$$

In a recently published paper<sup>1)</sup> I showed that a number of particularities of the vapour-pressure lines follow from these equations. Since then Mr. KATZ's investigations<sup>2)</sup> and the results communicated obtained was  $\frac{3}{2}R$ . It was mentioned during the discussion at the Conseil SOLVAY, Nov. 1911 that Professor KAMERLINGH ONNES and myself had undertaken an investigation of  $\gamma_{\Lambda}$  by KUNDT's method for hydrogen at temperatures down to that of liquid hydrogen, but this investigation has not yet been completed.

<sup>1)</sup> Zschr. f. phys. Ch. 75 p. 527.

<sup>2)</sup> These Proc. Vol. XIII p. 958.

in a paper by Mr. TIMMERMANS and myself <sup>3)</sup> have drawn my attention to some other conclusions from the formulae derived l. c. particularly with regard to systems the components of which differ much in vapour pressure. I shall deal with this in the following pages.

Let us first give the formulae which we shall want. A  $p, x_1$ -line will ascend or descend with increase of  $x_1$  according as  $\frac{dp_c}{dx}$  is positive or negative. Let us call the substance with the larger value of  $b$  the second component ( $x = 1$ ), and put:

$$b_2 = nb_1 \quad a_2 = k^2 a_1 \quad a_{12}^2 = l^2 a_1 a_2$$

$$\frac{b_{12} - b_1}{b_1} = g \quad \frac{b_2 - b_{12}}{b_2} = h \quad m_1 = \frac{T}{T_{k_1}} \quad m_2 = \frac{T}{T_{k_2}}$$

then

$$\left(\frac{dlp_c}{dx}\right)_{x=0} = -\frac{2f}{m_1}(kl-1-g) + 2(kl-1-2g) \quad . \quad . \quad (1)$$

$$\left(\frac{dlp_c}{dx}\right)_{x=1} = -\frac{2f}{m_2}\left(1-h-\frac{l}{k}\right) + 2\left(1-2h-\frac{l}{k}\right) \quad . \quad . \quad (2)$$

The question whether the  $p, x_1$ -line is concave or convex downward at the border, depends on the sign of  $\frac{d^2lp_c}{dx^2}$  in this way that  $\frac{d^2p}{dx_1^2}$  will have the same sign as  $\frac{d^2lp_c}{dx^2}$  for a line that ascends from the border, or if it descends so long as  $x_2 > \frac{1}{2}x_1$  resp.  $1-x_2 > \frac{1}{2}(1-x_1)$ . If  $x_2 < \frac{1}{2}x_1$  resp.  $1-x_2 < \frac{1}{2}(1-x_1)$ , the vapour-pressure line is convex when  $\frac{d^2lp_c}{dx^2}$  is negative, and concave when  $\frac{d^2lp_c}{dx^2}$  is positive. Also the stability or unstability of the liquid phases depends on this quantity. We are, namely, on the verge of stability when:

$$1 + x_1(1-x_1)\frac{d^2lp_c}{dx^2} = 0$$

So we are certain to be in the stable region everywhere where  $\frac{d^2lp_c}{dx^2}$  is positive; if on the other hand  $\frac{d^2lp_c}{dx^2}$  has a large negative value, then (for not too small value of  $x(1-x)$ ) we shall be in the unstable region, i.e. unmixing will take place. Expressed in the quantities defined just now we find for the required value at the two borders:

<sup>3)</sup> These Proc. Vol. XIII p. 865.

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=0} = -\frac{f}{m_1} \left\{ 2 + 8g^2 + 8g - \frac{d^2b}{dx^2} + 2k^2 - lk(4 + 8g) \right\} +$$

$$+ 4lk - 4l^2k^2 + 8g^2 + 2k^2 - 2 - 2 \frac{d^2b}{dx^2} \dots \dots \dots (3)$$

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=1} = -\frac{f}{m_2} \left\{ 2 + 8h^2 - 8h - \frac{d^2b}{dx^2} + \frac{2}{k^2} - \frac{l}{k}(4 - 8h) \right\} +$$

$$+ \frac{4l}{k} - \frac{4l^2}{k^2} + 8h^2 + \frac{2}{k^2} - 2 - 2 \frac{d^2b}{dx^2} \dots \dots \dots (4)$$

Now we arrive at a surprising result when we apply this formula to systems whose molecules differ much in size. If e.g.  $b_2$  is  $= 100 b_1$ , then  $\frac{b_{12}}{b_1}$  becomes  $= 22.4$  according to the well-known formula of LORENTZ; so  $g = 21.4$  and  $h = 0.776$ . If we further suppose  $k = 20$ , so that  $T_{k_2} = 4T_{k_1}$ ,  $p_{k_2} = \frac{1}{25} p_{k_1}$ , and  $m_2 = \frac{1}{4} m_1$ , equations (1) and (2) become:

$$\left(\frac{dlp_c}{dx}\right)_{x=0} = -\frac{2f}{m_1} (kl - 22.4) + 2(kl - 43.8) \dots \dots \dots (1a)$$

$$\left(\frac{dlp_c}{dx}\right)_{x=1} = -\frac{2f}{m_2} \left(0.224 - \frac{l}{k}\right) - 2\left(0.552 + \frac{l}{k}\right) \dots \dots \dots (2a)$$

So we find  $l = 1.04$  for the value of  $l$  which makes  $\left(\frac{dlp_c}{dx}\right)_{x=0}$  equal to 0 for a temperature  $m_1 = \frac{1}{2}$  and the supposition  $f = 7$ ; for smaller values of  $l$   $\left(\frac{dlp_c}{dx}\right)_{x=0}$  is then positive at this temperature, for larger values negative. Equation (2a) shows further that for values of  $l < 4$  the  $p, x$ -line ends descending for the second component. So  $\frac{dp}{dx}$  has the same sign on both sides for  $l = 1.05$ . But between a region of non-miscibility will be found. For with the values mentioned equation (3) passes into:

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=0} = -14 \{4525 - 3504 l\} + 80 l - 1600 l^2 + 4237 \dots \dots \dots (3a)$$

With a value of  $l$  in the neighbourhood of 1 the lefthand member becomes of the order  $10^{-1}$ ; so the curve is at first concave down-



ward, but already for a value of  $x$  of the order 0.0001 unstable states are reached. On the other hand equation (4) passes into:

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=1} = -56\{-0.507 + 0.1104l\} + 0.2l - 0.01l^2 + 0.581 \quad (4a)$$

and so this value becomes (with  $l$  about 1) of the order  $+20$ . So on the righthand side the  $p, x$ -line will be concave downward, and we shall have to get very far from the border before meeting with a region of unmixing.

If we put  $b_2 = 1000b$  instead of  $b_2 = 100b$ , we get the equations:

$$\left(\frac{dlp_c}{dx}\right)_{x=0} = -\frac{2f}{m_1}(kl-166) + 2(kl-331) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

$$\left(\frac{dlp_c}{dx}\right)_{x=1} = -\frac{2f}{m_2}\left(0.166 - \frac{l}{k}\right) - 2\left(0.668 + \frac{l}{k}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=0} = -\frac{f}{m_1}(217800 + 2k^2 - 1324lk) + 4lk - 4l^2k^2 + 2k^2 + 215000. \quad (3b)$$

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=1} = -\frac{f}{m_2}\left\{0.45 + \frac{2}{k^2} + 2.67\frac{l}{k}\right\} + 4\frac{l}{k} - 4\frac{l^2}{k^2} + \frac{2}{k^2} + 0.89. \quad (4b)$$

and if we now suppose  $k = 63$ , so that again  $T_{k_2} = 4T_{k_1}$ , all our conclusions remain of force, and the peculiarities which we pointed out (insolubility on the side of the small molecule etc.) are still more pronounced. And also values of  $\frac{b_2}{b_1}$  considerably smaller than 100 still yield the same results.

Summarising them we must say that for the systems considered with a value of about  $l = 1$  the  $p, x_1$ -line begins at the side of the small molecules slightly ascending concave downward, that, however, already with exceedingly small concentration a region of unmixing is reached, which lies very asymmetrically in the lefthand side of the figure, and that the  $p, x_1$ -line after having left this region of unmixing, continually descending and finally convex downward reaches the line for the second component.

## § 2. *The experimental results of Mr. KATZ.*

Now it is very remarkable, that this course entirely agrees with that of the vapour-pressure lines determined by Mr. KATZ for the majority of "swelling" bodies, those with limited imbibition power. Here too on the side of water an exceedingly small line (generally so small that it cannot even be determined experimentally) is found for the solution of the swelling substance in water, and on the other

side of this very asymmetrically situated region of unmixing just such a line as was described just now.

No doubt we are not justified in concluding from this agreement that the substances to which Mr. KATZ's figures refer, satisfy all the conditions that we had to put in order to be able to arrive at our conclusions; to apply the law of corresponding states to casein and haemoglobin must certainly be called a very bold generalisation, even apart from the other suppositions on which our formulae are founded. Still I thought this agreement striking enough to justify a closer investigation for the solution of the question in how far the experimental particularities found by Mr. KATZ would have to be expected in virtue of the simplest theory for a mixture of two perfectly normal components, when the ratio between the size of the molecules,  $b_2/b_1$ , becomes very great. Mr. KATZ was so kind as to summarize the results of his measurements for me as follows:

1. If we draw the water-vapour tension of the swelling substance as function of the molecular percentage (VAN DER WAALS's  $p, x$ -curve), we get a line which (cf. fig. 1, which represents the line for inulin in proper proportions<sup>1)</sup>):

*a.* lies for not very small values of  $x$  (pure water) under the value which the vapour tension would have if VAN 'T HOFF's law  $p = p_1(1 - x)$  held for all concentrations.

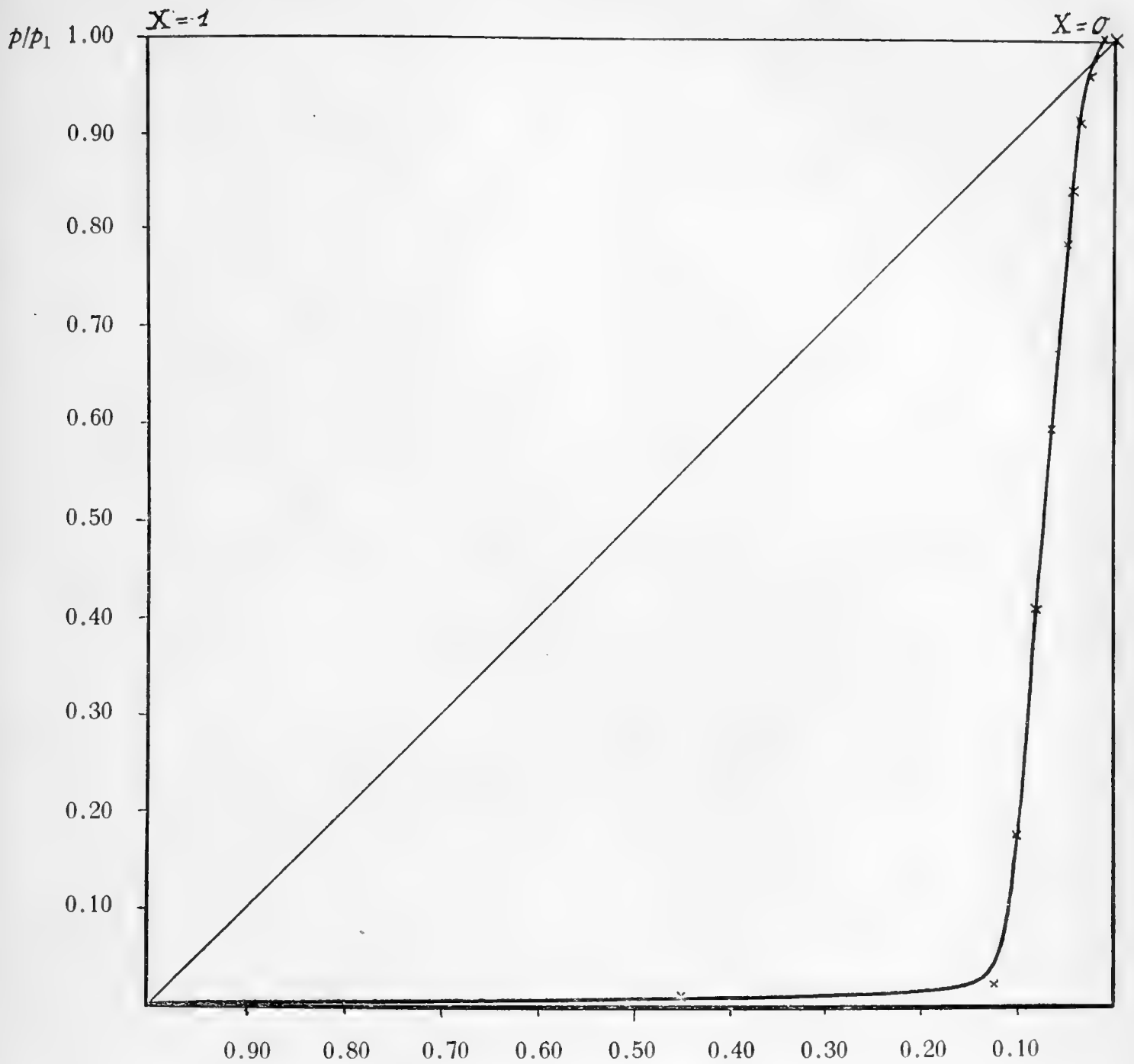
*b.* begins almost horizontally for  $x$  about 1, and does not begin to rise abruptly until past  $x = 1/2$ .

*c.* turns its convex side downward for  $x$  about 1, then gets a point of inflection (for smaller  $x$ ), and finally turns its concave side downward for very small value of  $x$ .

*d.* presents an excentrically situated region of unmixing for very small  $x$ , so excentrically as has not been observed anywhere else as yet. Pretty well pure water  $x = 0.00001$  coexists with  $x = 0.002$  or 0.006. The lines for casein (albumen) and inulin (polysaccharide) may serve as an example. For both substances the minimum molecular weights have been taken (casein = 4000, inulin = 1800) in all these calculations. If higher values are used, the above-mentioned properties are even more pronounced.

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<sup>1)</sup> In this figure of Mr. KATZ the component with the smaller molecule (water), has, however, been thought on the right hand, whereas in the text it has been assumed, where the contrary has not been expressly stated, that the molecular weight increases from left to right.



<i>Inulin</i>		<i>Casein</i>	
$x$	$p/p_1$	$x$	$p/p_1$
0.007	1	0.004	1
0.024	0.962	0.014	0.962
0.034	0.914	0.018	0.917
0.041 <sup>s</sup>	0.853	0.021	0.853
0.049	0.788	0.024	0.788
0.063	0.596	0.031	0.596
0.079	0.410	0.041	0.410
0.100	0.176	0.062	0.176
0.125	0.022	0.178	0.022
0.45	0.01	0.29	0.01

2. The heat of mixing (generation of heat when 1 gr. of dry substance absorbs  $i$  gr. of water) is *strongly positive*, and is very well rendered by a hyperbola:

$$W = \frac{Ai}{B+i}.$$

3. The volume contraction  $c$  by the mixing (in  $\text{cm}^3$ . when 1 gr. of dry substance absorbs  $i$  gr. of water) is strongly positive, and follows a line which closely resembles a hyperbola.

4. If we compute  $\frac{c}{W}$  for small  $i$ 's (*lim.*  $i = 0$ ), we find that this quotient is of the same order of magnitude for the most different swelling substances viz. between 10 and  $25 \times 10^{-4}$ , and that this quotient is of the same order of magnitude as for mixtures of sulphuric acid, phosphoric acid, and glycerin with water.

The analogy of the latter substances with the swelling substances is the more striking, because they present all the properties described under 1 ( $a$ ,  $b$ , and  $c$ ), under 2 and under 3 exactly as for the swelling substances. There is only one difference: they are miscible in all proportions, whereas some swelling bodies exhibit the characteristically excentric region of unmixing described under 1  $d$ . Other swelling substances have an unlimited power of imbibition, but behave for the rest as described above. So this difference will not be essential.

Limited or unlimited miscibility, it seems, may depend on small factors, as closely allied substances may belong to different types. Further quantitatively there exists this difference that for the swelling substances the vapour pressure line begins to ascend much less steeply, the lines for the volume contraction and for the heat of mixing on the other hand much more steeply than in the usual case. We may express the latter also in this way that for swelling substances the quantity  $b$  in the equation of the hyperbola for the volume contraction  $c = \frac{ai}{b+i}$  is remarkably small, just as the quantity  $B$  in the formula of the heat of mixing.

§ 3. *The integral equation of the vapour pressure line.* Let us begin our investigation with the vapour pressure lines. To investigate whether they agree with the experimentally determined ones also with respect to the peculiarities not yet treated in § 1, it is easier to use the integral relation between  $p$  and  $x$  instead of the differential

relation used there. We find for this <sup>1)</sup>, when the vapour pressure of the second component may be neglected which is certainly the case here:

$$p = p_1 (1 - x) e^{-\left\{ \log p_1 - \left( \log p_c - x \frac{d \log p_c}{dx} \right) \right\}} = p_1 (1 - x) y$$

So everywhere, where the exponent of  $e$  is positive, the vapour pressure line lies below the straight line which would represent the vapour pressure when the law of VAN 'T HOFF held for all concentrations. When this exponent is negative the real vapour pressure lies below this straight line. If we now apply VAN DER WAALS'S formula for  $p_c$ , and if we assume as above  $b_2 = 100 b_1$ ,  $b_{12} = 22,4 b_1$ ,  $a_2 = 100 a_1$ ,  $a_{12} = 20 a_1$  we get:  $y = 10^{-4}$  for  $x = 0.5$  and  $y = 0.25$  for  $x = 0.2$ . So we really see the same course as given under  $a, b$ , and  $c$  <sup>2)</sup>. But on these suppositions the region of unmixing is not so narrow as is required in  $d$ . For  $y$  becomes  $= 2.5$  for  $x = 0.1$ , and as for absolutely stable states the vapour pressure in the mixture cannot be greater than the sum of the vapour pressures of the components <sup>3)</sup>, we must be in the region of unmixing already here.

If, however, we take  $a_2 = 1000 a_1$  and  $a_{12} = 25 a_1$ , we get  $y = 0.1$  for  $x = 0.1$  and  $y = 1.22$  for  $x = 0.01$ . If  $\frac{b_2}{b_1}$  is still greater than 100, we may even find much narrower regions of unmixing. Thus e.g.  $y = 0.95$  for  $x = 0.01$  with  $\frac{b_2}{b_1} = 1000$  and the corresponding  $\frac{b_{12}}{b_1} = 166$ , while  $a_2$  is put  $= 10000 a_1$  and  $a_{12} = 105 a_1$ . That there exists still a region of unmixing, however, appears from the value  $y = 1,04$  for  $x = 0.001$ . If  $a_{12}$  is taken somewhat greater still, the region of unmixing disappears.

<sup>1)</sup> Compare the second volume of the Lehrbuch der Thermodynamik, which will shortly appear, p. 178.

<sup>2)</sup> That a point of inflection must occur follows from the fact that the vapour-pressure line is turned convex downward at first, and then concave downward in the region of unmixing, as it has a maximum there. No general rule can, however, be derived as to whether this point of inflection will still lie in the absolutely stable, or in the metastable region. In virtue of the very slight breadth of the plait, however, which leads us to expect that we are already quite close to the maximum of the vapour-pressure line on the verge of unmixing it may be considered as exceedingly probable that the point of inflection still falls in the absolutely stable region.

<sup>3)</sup> Cf. the footnote p. 111.

We shall presently return to these results, but we may now already state that with suitable values of  $a_{12}$  and  $a_1$  really vapour pressure lines are obtained which perfectly agree in type with the experimentally determined ones. It deserves notice that this result is in the first place the consequence of the great value which  $\frac{d^2b}{dx^2}$  assumes according to our suppositions (great value of  $\frac{b_2}{b_1}$  and validity of LORENTZ'S formula for  $b_{12}$ ). If we take  $b$  as linear function of  $x$ , as is often permissible for small values of  $\frac{b_2}{b_1}$  nothing remains of these results. The obtained vapour-pressure lines are namely characterised by this that  $\mu''_x$  is strongly positive for values of  $x$  near 1, which leads to the strongly convex  $px$ -line, whereas near  $x = 0$   $\mu''_x$  is strongly negative, which circumstance gives rise to the region of unmixing. If, however, we take  $b$  as linearly dependent on  $x$ , change of sign of  $\mu''_x$  becomes impossible<sup>1)</sup>. This quantity must have the same sign throughout the whole breadth of the figure; then we can have unmixing with negative value of  $\mu''_x$ , but then the vapour pressure line ends also concave downwards on the side of the slight vapour pressures. This is accompanied by an extension of the region of unmixing over the full width of the figure as in the case of mercury-water. When the vapour-pressure line ends concave downward, however, on the side of the small vapour pressures,  $\mu''_x$  must be positive, and then unmixing is impossible. And this holds whatever values one may choose for  $a_2$  and  $a_{12}$ . Only for very large values of  $\frac{d^2b}{dx^2}$  as they follow from the formula of LORENTZ for great values of  $\frac{b_2}{b_1}$  a region of unmixing can occur in a  $px$ -line which is convex on the other side. *Whether* this region of unmixing then occurs, and how wide it will be, will depend on the  $a$ 's, and more particularly on the ratio of  $\frac{a_{12}}{a_1}$ . We have seen this already in the foregoing discussion, and we shall find confirmed in what follows that only a very small change of this quantity is required to make a mixture with an exceedingly narrow region of unmixing on the side of the small molecule pass into a system that is miscible over its full breadth. This is in accordance with Mr. KATZ'S remark "limited or unlimited miscibility, it seems, may depend on small factors, as closely allied

<sup>1)</sup> Cont. II, p. 152.

substances may belong to different types". Of course it would be entirely premature now that we are still altogether ignorant about the causes that govern the value of the quantity  $\frac{a_{12}}{a_1}$  even for the best known systems, to pronounce an opinion about the question why for some systems the value is such that a very narrow region of unmixing appears, whereas for others there exists complete miscibility. Even quite apart from the fact that it does indeed follow from what precedes and what follows that the experimental peculiarities found by Mr. KATZ can all appear for perfectly normal substances, but that it does not follow by any means, of course, that not all kinds of other circumstances might be found for the systems investigated by him, which do not affect the general character of the lines, but might have a very considerable influence on the numerical values of the quantities to be calculated. For this reason I have abstained from endeavours to find the numerical values of  $a$ 's and  $b$ 's, and have confined myself to the general course of the investigated lines.

§ 4. *The volume-contraction.* Further on we shall return to the vapour-pressure lines, but for a reason which will soon become clear, we shall first speak about the volume contraction. According to Mr. KATZ it may be represented by a hyperbola:

$$c = \frac{ai}{b+i}$$

in which  $c$  is the contraction in  $cm^3$  when 1 gr. of dry substance absorbs  $i$  gr. of water. What does the theory of the normal mixtures teach us about this quantity? If we may assume that the temperature has been chosen so low that we may put the limiting volume  $b$  for the liquid volume, the increase of volume  $\Delta v$  in consequence of the mixing of  $M_1(1-x)$  gr. of water and  $M_2x$  gr. of dry substance becomes:

$$\Delta v = b_x - b_1(1-x) - b_2x = -x(1-x)(b_1 + b_2 - 2b_{12}) \quad (5)$$

From this we must derive the relation between  $c$  and  $i$ . Now evidently:

$$c = -\frac{\Delta v}{M_2x}$$

follows from the definitions,  $c$  and  $\Delta v$  taken for the same concentration.

If we further mix 1 gr. of dry substance and  $i$  gr. of water resp.  $M_2$  with  $M_1$   $i$  gr., the number of molecules are evidently in the ratio  $1 : \frac{M_2}{M_1}i$  so:

$$x = \frac{1}{1 + \frac{M_2 i}{M_1}} = \frac{M_1}{M_1 + M_2 i} \dots \dots \dots (6)$$

and

$$1 - x = \frac{M_2 i}{M_1 + M_2 i}$$

So equation (5) becomes :

$$c = \frac{i}{M_1 + M_2 i} (b_1 + b_2 - 2b_{12})$$

so really a hyperbola.

Also the second above mentioned peculiarity of the  $c, i$ -lines that the quantity  $b$  in the equation of the hyperbola becomes much smaller than is usually the case, is found confirmed here. For  $\frac{M_1}{M_2}$  is found for this quantity.

*The heat of mixing.* Mr. KATZ has already pointed out <sup>1)</sup>, that the hyperbola found by him is in accordance with a formula given by VAN DER WAALS in the *Théorie Moléculaire*. But this formula was derived on the supposition of linear dependence of  $b$  on  $x$  ( $b_1 + b_2 = 2b_{12}$ ) and we saw already that both the experimental vapour pressure and volume contraction lines and the theory exclude this supposition in our case. If we, however, again assume the supposition, on which the said formula of VAN DER WAALS is also founded, that viz. the potential energy of a mixture may be represented by  $-\frac{a_x}{b_x}$ , we find for the increase of the potential energy or the absorbed quantity of heat when  $M_2 x$  gr. of dry substance is mixed with  $M_1 (1-x)$  gr. of water :

$$A = \frac{x(1-x)}{b} \left\{ 2a_1 \frac{b_{12}}{b_1} + a_2 \frac{b_1}{b_2} - 2a_{12} - a_1 - x \left( \frac{a_2}{b_2} - \frac{a_1}{b_1} \right) (b_2 + b_1 - 2b_{12}) \right\} (7)$$

Between  $A$  and the quantity  $W$  used by Mr. KATZ the relation  $W = -\frac{A}{M_2 x}$  exists again, and of course, equation (6) holds again. So it appears that we do not get a hyperbola for  $W$ , but a curve of higher degree than the second.

In how far this involves a deviation from the experimental data, we shall examine presently ; first we must see what conclusion may be derived from the limiting ratio  $\frac{c}{W}$  for very small values of  $i$

<sup>1)</sup> l. c. p. 970.



determined by Mr. KATZ, so values of  $x$  which are nearly equal to 1. With such values of  $x$  the terms multiplied by  $(b_2 + b_1 - 2b_{12})$  now predominate on the lefthand side; so we find for the required ratio:

$$\frac{A}{\Delta v} = \frac{\frac{a_2}{b_2} - \frac{a_1}{b_1}}{b_2}$$

If this expression is to be independent of the order of magnitude of  $b_2$ , we must conclude that in general  $a$  increases proportionally with  $b^2$  for increasing values of  $b$ , so that  $\frac{a}{b^2}$  remains of the same order of magnitude.

Also with  $a$  proportional to  $b$  the coefficients  $\frac{A}{\Delta v}$  would remain equal, they all being zero then. This supposition does not call for any further discussion, also because the critical temperature rapidly rises for all known bodies with great increase of  $b$ , whereas the critical pressure remains of the same order of magnitude.

§ 5. *Supposition that  $\frac{a}{b^2}$  is of the same order of magnitude for the components.* So we should have to conclude from this that we have assumed the increase of  $a$  for certain increase of  $b$  too small in § 1 and 3. And now the question should be solved whether what was found above for the vapour-pressure line continues to hold also with the now supposed great increase of  $a$ . For this purpose I once more examined the course of the vapour-pressure line with the aid of the above formula, now on the suppositions  $b_2 = 100 b_1$ ,  $b_{12} = 22.4 b_1$ ,  $a_2 = 10000 a_1$ . For  $a_{12} = 150$  we find then that the region of unmixing has quite disappeared; with  $a_{12} = 140$  on the other hand we find  $y = 1.03$  for  $x = 0.01$ . So if we take  $x$  slightly higher, we shall find exactly the required width of the region of unmixing already with  $\frac{b_2}{b_1} = 100$ . So all Mr. KATZ's results mentioned under 1, 3, and 4 can be derived from our theory.

So it finally remains the question in how far the result under 2 is incompatible with the simplest theory developed here. If we take the last mentioned example, viz.  $b_2 = 100 b_1$ ,  $b_{12} = 22.4 b_1$ ,  $a_2 = 10000 a_1$  and  $a_{12} = 140 a_1$ , we find for the heat of mixing the expression:

$$A = - \frac{x(1-x)}{b_x} (1362 + 5563.8x) \dots \dots \dots (7a)$$

This is in conflict with the hyperbolic line  $W = \frac{Ai}{B+i}$ , for this leads to an expression of the form :

$$A = -\frac{x(1-x)}{C+Dx} \dots \dots \dots (8)$$

For a course from  $x = 0$  to  $x = 1$  equations of these two types can certainly not perfectly accurately agree; it is, however, the question in how far they deviate within the region in which the observations lie ( $x = 0.1$  to  $x = 0.4$ ). If now for  $x = 0.1, 0.2, 0.3, 0.4$  we calculate the value of the expression  $\frac{b_x}{136.2 + 5563.8x}$ , and if we divide the result by the value for  $x = 0.4$ , we find :

$$0.7342, 0.8223, 0.9110 \text{ and } 1.0000$$

these values do not ascend linearly, but they differ from the purely linearly ascending ones :

$$0.7336, 0.8223, 0.9110, 0.9997$$

everywhere less than 1‰, the experimental errors certainly amounting to a few percentages. So it is clear that the discrepancies which exist between a formula of the type (7) and of the type (8), are much too small in the considered region to allow of an experimental decision. We must conclude that a formula of type (7) represents the experimental data as well as a formula of type (8)<sup>1)</sup>. Farther reaching conclusions are of course excluded, as we already remarked

<sup>1)</sup> Perhaps we may go still further and say that in the general case a formula as (7) represents the experimental relations *better* than (8). For according to the latter formula the total heat of mixing  $W$  and also the differential heat of mixing  $\frac{dW}{di}$  must always retain the same sign, while on the other hand for certain values of the  $a$ 's and  $b$ 's a reversal of sign is possible according to formula (7). And this change of sign of  $\frac{dW}{di}$ , which can never take place for a hyperbolic formula, seems indeed to appear in reality in some cases e.g. for inulin, as appears from the subjoined table.

$i$	$W$ in Cal.
0	0
0.052	11.8
0.095	16.7
0.116	19.0
0.223	22.4
0.293	23.0
1.05	21.8

It is also in connection with this deviation of the theoretically required formula

above, by the absence of accurate numerical values of all the  $a$ 's,  $b$ 's, and even the molecular weights.

So summarizing we must say that *all* the experimentally found particularities can appear exactly in the same way for mixtures of perfectly normal substances which behave according to the simplest theory.

§ 6. *Deviation from the law of VAN 'T HOFF even in case of extreme dilution.* There is another particularity in connection with the absence or presence of unmixing, to which it may be desirable to draw attention. I mean departures from the well-known vapour-pressure formula of VAN 'T HOFF for extreme dilutions

$$\frac{dp}{pdx_1} = -1.$$

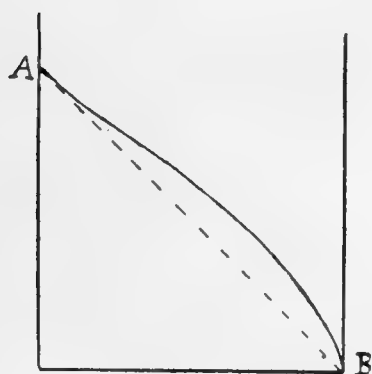


Fig. 3.

This formula, which may be expressed geometrically by saying that the vapour-pressure line<sup>1)</sup> in its limiting direction points to the opposite angle (direction  $AB$  in figure 3), is considered of general validity for systems whose components differ widely in volatility. And indeed if we understand by this latter condition that  $\frac{x_2}{x_1} = 0$ , at the limiting value,

from a hyperbola that the property mentioned in the last lines of § 2 can be cal.

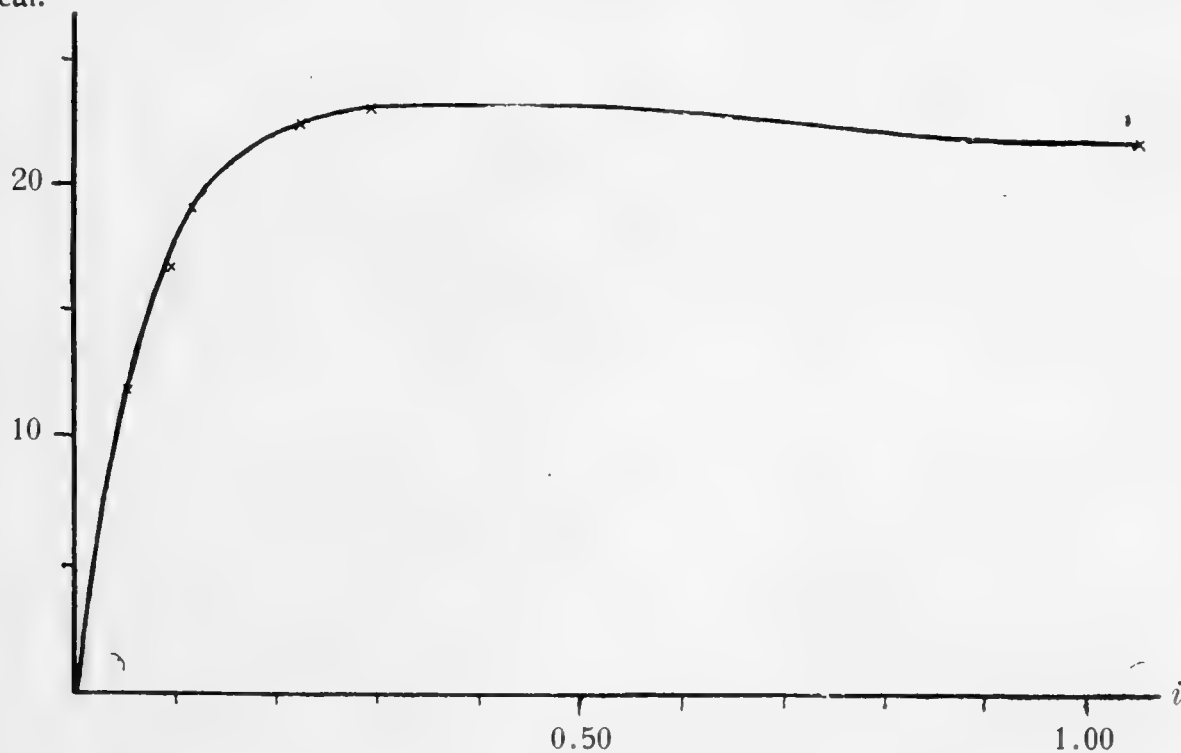


Fig. 2.

proved in a simple way for the volume contraction, but not for the heat of mixing.

<sup>1)</sup> Of course the *total* vapour-pressure line is meant here. For the partial vapour

i. e. that the ratio of the concentration of the second component in the vapour and in the liquid is very small, this rule can be perfectly rigorously derived for the limiting value purely thermodynamically in the wellknown way. Purely thermodynamically, because we have then only to do with the logarithmic part of the thermodynamic functions, and need not know anything more about the system. But this definition of "difference in volatility" is not the only possible one, and not the only one that naturally suggests itself. We might as well, perhaps better, understand by this idea, that one pure component has a very much lower vapour-pressure than the other at a definite temperature. And these two definitions by no means always coincide. Let us e. g. take a system for which the equations 1—4 hold. On the supposition  $f=7$  and  $T_{k_2}=\frac{1}{2}T_{k_1}$  it follows that the quantity  $p_2/p_1$  is of the order  $10^{-18}$  at a temperature of  $\frac{1}{2}T_{k_1}$ . So there seems, indeed, to be every reason to say that the second component is much less volatile than the first. Yet by no means

$\lim. \frac{x_2}{x_1} = 0$ . On the contrary, if we put  $l=1$ , it follows from the

above that the  $p_1x_1$ -line begins ascending, so  $x_2 > x_1$ ; in the beginning the second component is present in the vapour in greater quantity than in the liquid, and VAN 'T HOFF'S law by no means holds any longer even for the extremest dilutions. Exactly the same thing

applies for other values of  $\frac{b_2}{b_1}$ . So we must supplement the condition

for the validity of VAN 'T HOFF'S law also for the extremest dilutions as follows, that the components differ greatly in vapour-pressure, and that *there be no region of unmixing in the neighbourhood*. For if this were not the case we should already soon get a vapour in which the partial pressure of the second component would be greater than the total pressure of the component at the chosen temperature, and this is not possible for absolutely stable states<sup>1)</sup>. So where the rule of VAN 'T HOFF does not hold with great difference in vapour pressure, this will be in the closest connection with this

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pressure lines on the side of their component it *always* holds that they point to the opposite angle with their initial direction, as immediately follows by differentiation of the equation on p. 103.

1) We used this thesis already above to conclude to the existence of unmixing. It may be proved as follows. It follows from the differential equations of the two partial vapour-pressure lines (Cont. II, p. 163) that they will possess a maximum or a minimum only on the borders of the stable and unstable region. So if there is no unmixing, the partial vapour-pressure line of the first component is always descending, that of the second always ascending. If there is a region of unmixing,

that the liquid phase becomes unstable and unmixing appears already at very slight concentrations. So we shall have to expect that VAN 'T HOFF'S law does hold for substances with unlimited imbibition power. And our formulae prove in harmony with this. As we namely saw it is required e.g. in the case  $b_2 = 100 b_1$  and  $l$  not far from 1 that  $\frac{a_2}{a_1}$  does not lie far below 35. Then, however, we find for  $\frac{dlp_c}{dx}$  about  $-380$ , and so  $\lim \frac{a_2}{a_1}$  of the order  $10^{-150}$ . On the other hand for substances with limited imbibition power VAN 'T HOFF'S law *may* hold, but this is by no means necessary, or even probable, and we shall undoubtedly have to take this circumstance into account in attempts to derive the molecular weight of these substances from the properties of their solutions.

§ 7. *Other systems with great difference in vapour pressure of the components.* I already pointed out the possibility of such departures from VAN 'T HOFF'S rule in an earlier communication published in These Proceedings, mentioned in the beginning of this paper. What was said there, will have been made sufficiently clear by the foregoing discussion. So I shall only add a few calculations here for systems as the one discussed there (aniline or nitrobenzene with isopentane or hexane). These systems agree in so far with the systems discussed in the foregoing that there exists a very large difference in vapour pressure between the two components, though not nearly so great as in the cases examined by Mr. KATZ, where the second component nowhere shows a measurable vapour pressure. But for the rest the difference is great; whereas in the systems discussed up to now the ratio  $\frac{b_2}{b_1}$  reaches very great values, the ratio here is not far from 1,

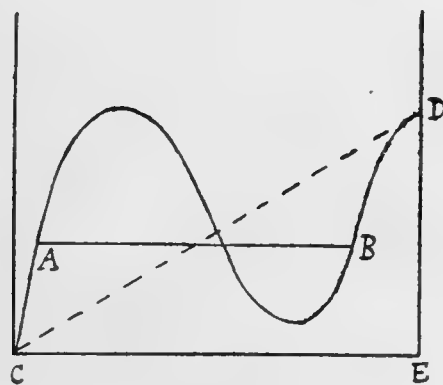


Fig. 4.

the partial vapour pressure of a component in the maximum can of course considerably rise above the value for the component itself (see fig. 4), but then this is always in the metastable or unstable region. For the partial vapour pressures must be the same in the two coexisting liquid phases. So the point *A* must lie on the same level as *B*, and as both between *A* and *C*, and between *B* and *D* the partial vapour pressure line can only be ascending, the partial vapour pressure must be smaller than *DE* throughout the region of the absolute stable mixtures.

and the substance with the greater vapour pressure has here even the greater molecule. Instead of in the righthand half of the general isobaric figure of VAN DER WAALS we are now in the lefthand part. Accordingly the unmixing found here must not be ascribed to the same cause, the high value of  $\frac{b_2}{b_1}$ , but (so long as we assume that we have not to do with abnormal systems, and with the systems mentioned we may do so to all probability) to a smaller value of  $l$  than generally occurs.

Let us take as an example the system aniline-hexane.  $b_1$  is here 0,006113,  $\frac{b_2}{b_1} = 0,007849$ , so  $b_2 = 1,284$ , and  $\frac{b_{12}}{b_1} = 1,136$  follows

from the formula of LORENTZ, so  $h = 0,1153$ , and  $\frac{d^2b}{dx_2} = 0,017$ .

Further  $a_2 = 0,04928$  and  $a_1 = 0,05282$ , so  $k = 0,9659$ . If we substitute these values in the equations (2) and (4), we get:

$$\left(\frac{dlp_c}{dx}\right)_{x=1} = -\frac{2f}{m_2}(0,8847 - 1,035l) + 2(0,7694 - 1,035l). \quad (2c)$$

and

$$\left(\frac{d^2lp_c}{dx^2}\right)_{x=1} = -\frac{f}{m_2}(3,31 - 3,19l) + 4,14l - 4,29l^2 + 0,22. \quad (4c)$$

So we get  $\left(\frac{d^2lp_c}{dx^2}\right) = -1,2$  for  $l = 1$  with  $f = 7$  and  $m_2 = \frac{2}{3}$  ( $T_k$  hexane =  $235^\circ$  and the temperature of the upper mixing point =  $68^\circ,9$ ). So we have not to expect unmixing, at least in the neighbourhood of the border, nor for greater concentrations, because  $\frac{d^2lp_c}{dx^2}$  must at least be  $-4$  to make  $1 + x(1-x)\frac{d^2lp_c}{dx^2}$

negative. In agreement with the complete miscibility  $\frac{dlp_c}{dx} = 2,62$ , and so

$\frac{1-x_2}{1-x_1} = \frac{1}{10}$ , and accordingly VAN 'T HOFF'S law is fulfilled

with pretty close approximation. As soon, however, as  $l$  becomes smaller, this is changed. For  $l = 0,9$  we get  $\frac{dlp_c}{dx} = 0,66$ , and so

$\frac{1-x_2}{1-x_1} > \frac{1}{2}$ , and the lowering of the vapour pressure of the second

component by addition of the first will therefore amount to only half of what VAN 'T HOFF'S rule would require. But as  $\frac{d^2lp_c}{dx^2}$  has the

value  $-4,08$  already now, we see clearly that there is a region of unmixing at hand, and it will already have appeared with some decrease of temperature. For  $l = 0,85$  finally  $\frac{dlp_c}{dx}$  has already got the negative sign  $\left(\frac{dlp_c}{dx} = -0,3\right)$  at the chosen temperature; so the vapour-pressure line does not descend from the side of the most volatile component, but ascends; there is a maximum vapour pressure. But then the value of  $\frac{d^2lp_c}{dx^2}$  has fallen to almost  $-6$ , and we may expect that even for not very great concentrations unmixing will take place.

The calculations given here, will, I hope, have sufficiently elucidated the thesis which I pronounced in the cited paper that VAN 'T HOFF'S rule need not hold, even as a limiting law, for systems whose components differ very much in vapour-pressure, when viz. these substances do not mix in all proportions, or at least a region of unmixing is close at hand. They also set forth again <sup>1)</sup>, how much greater the influence is of slight deviations in the value of  $l$  from unity, than in those of  $\frac{b_2}{b_1}$  or  $\frac{a_2}{a_1}$  and that such deviations are able to modify the course of phenomena entirely, so that certainly only a small part of all the possible cases is observed when we start from the supposition that the relation  $l = 1$  should be always rigorously fulfilled. On the other hand they also show that in all the systems known to us, we have to do with values of  $l$  which are contained within narrow limits, and that we have not a single indication to think values possible for the value of  $l$  of the same order as undoubtedly occur for  $\frac{b_2}{b_1}$  and also for  $\frac{a_2}{a_1}$ .

**Mathematics.** — “*On looping coefficients.*” By DR. L. E. J. BROUWER.  
(Communicated by Prof. D. J. KORTEWEG.)

(Communicated in the meeting of February 24, 1912).

Let us suppose in  $Sp_3$  two non-intersecting simple closed curves  $k_1$  and  $k_2$  furnished with a sense of circuit. Then  $k_1$  possesses with respect to  $k_2$  a *looping coefficient* answering to the intuitive notion

<sup>1)</sup> Cf. the paper in the Zsch. f. phys. Ch. 75 cited in the beginning of this treatise.

of the *number of times that  $k_1$  circulates around  $k_2$* , and generally defined as  $\frac{1}{4\pi} \times$  the variation corresponding to a circuit of  $k_1$  of the solid angle projecting  $k_2$  out of a variable point of  $k_1$ .

A first objection to this definition is, that without further agreement it can be applied only to special categories of simple closed curves. For, as soon as e.g. a simple closed curve  $k$  intersects of a sheaf  $s$  all the rays contained in a certain finite solid angle, the solid angle projecting  $k$  out of the vertex of  $s$ , has no more a definite value.

A second objection to the definition is, that it cannot be generalized to a notion of "*looping coefficient in  $Sp_n$  of a two-sided closed  $Sp_h$  with respect to a two-sided closed  $Sp_{n-h-1}$  not intersected by  $Sp_h$ .*"

In the following we shall give a definition for which these two objections have been annulled.

### § 1.

On each of the two curves  $k_1$  and  $k_2$  we construct a *scale of measurement*<sup>1)</sup>, and we consider the set  $R$  of pairs of points consisting of a point of  $k_1$  and a point of  $k_2$ . A part of  $R$  determined by an element<sup>2)</sup> of  $k_1$  and an element of  $k_2$  we shall call a *paralleloelement*. It appears as a continuous one-one image of a parallelogram. Each of these image parallelograms can be divided into four triangles with a common vertex inside the parallelogram and with their bases in the sides of the parallelogram. Accordingly we can divide each paralleloelement of  $R$  into four two-dimensional elements, and with this we attain that the whole set  $R$  is divided into two-dimensional elements which by their mode of being joined cause  $R$  to appear as a *closed two-dimensional space*.<sup>3)</sup>

Let  $p$  be a paralleloelement of  $R$ ,  $d_1$  resp.  $d_2$  the corresponding element of  $k_1$  resp.  $k_2$ ,  $A_1$  resp.  $B_1$  the negative resp. positive endpoint of  $d_1$ ,  $A_2$  resp.  $B_2$  the negative resp. positive endpoint of  $d_2$ , we then define the row of pairs of points  $(A_2A_1)$ ,  $(A_2B_1)$ ,  $(B_2B_1)$  as a positive indicatrix of the *partitional simplex*<sup>4)</sup> of  $p$  determined by those pairs of points, and with the aid of it we fix the positive indicatrix of the four elements of  $R$  belonging to  $p$ <sup>5)</sup>. In this way we determine of all elements of  $R$  the positive indicatrix, where for

1) Mathem. Annalen 71, p. 98—100.

2) *ibid.*, p. 97.

3) *ibid.*, p. 98.

4) *ibid.*, p. 100.

5) *ibid.*, p. 101.



two arbitrary elements having a side in common these indicatrices satisfy the relation prescribed for *two-sided* spaces <sup>1)</sup>.

So  $R$  is a *closed two-sided two-dimensional space*.

The set of the vector directions of  $Sp_3$  forms likewise a closed two-sided two-dimensional space (of the connection of the sphere) which we shall represent by  $B$ . The positive indicatrix of the spheres of  $Sp_3$  (and with it at the same time the positive indicatrix of  $B$ ) we determine by regarding them as boundary of their inner domain <sup>2)</sup>.

If we conjugate to each pair of points consisting of a point of  $k_1$  and a point of  $k_2$  the direction of the vector connecting the two points, we determine a *continuous one-one representation  $\alpha$  of  $R$  on  $B$* . To this representation belongs a finite integer  $c$  independent of the mode of measurement of  $R$ , and therefore also of the mode of measurement of  $k_1$  and  $k_2$ , which is called the *degree* of the representation, and possesses the property that the image of  $R$  covers positively each partitional domain of  $B$  in toto  $c$  times <sup>3)</sup>.

It is this degree of representation which we define as the *looping coefficient of  $k_1$  with respect to  $k_2$* .

By exchange of  $k_1$  and  $k_2$  we find that on one hand the indicatrix of  $R$  changes its sign, but on the other hand each image point on  $B$  is replaced by its opposite point. So the *looping coefficient of  $k_2$  with respect to  $k_1$  is equal to the looping coefficient of  $k_1$  with respect to  $k_2$* .

We shall now show that for rectifiable curves the looping coefficient of  $k_1$  with respect to  $k_2$  can be expressed by the formula:

$$\frac{1}{4\pi} \int \text{Vol. prod. } (ds_1, ds_2, r^{-2}) \dots \dots \dots (1)$$

This integral namely can be interpreted for rectifiable curves as follows: We construct in  $k_1$  resp.  $k_2$  a simplicial division <sup>4)</sup>  $z_1$  resp.  $z_2$ . To this corresponds a simplicial division  $z$  of  $R$ , whose base simplexes <sup>5)</sup> are determined in connection with the base arcs <sup>6)</sup> of

<sup>1)</sup> *ibid.*, p. 101.

<sup>2)</sup> *ibid.*, p. 108.

<sup>3)</sup> *ibid.*, p. 106.

<sup>4)</sup> *ibid.*, p. 101.

<sup>5)</sup> That here the base simplexes are found by division of a paralleloelement, not as i. e. by division of an element, has of course no influence on our reasoning. Moreover, after HADAMARD (comp. J. TANNERY, "Introduction à la théorie des fonctions d'une variable", Vol. II, p. 463) a simplicial division of the paralleloelements can be subdivided to a simplicial division of the elements.

<sup>6)</sup> i. e. one-dimensional base simplexes.

$k_1$  and  $k_2$  in the same way as we have determined above the elements of  $B$  in connection with the elements of  $k_1$  and  $k_2$ . Each base arc of  $z_1$  resp.  $z_2$  we replace by the corresponding "chord", i. e. by the straight line segment with the same endpoints. Let  $\alpha_1$  be the chord corresponding to the base arc  $\beta_1$  of  $k_1$ ,  $\alpha_2$  the chord corresponding to the base arc  $\beta_2$  of  $k_2$ ,  $r$  the distance of their midpoints, then  $\alpha_1$  and  $\alpha_2$  regarded as vectors determine together with a vector of size  $r^{-2}$  in the direction of the straight line connecting their midpoints, a certain volume product. Of the volume products appearing in this way for the different pairs  $(\alpha_1, \alpha_2)$  we take the sum  $S$ ; our integral is to be regarded as  $\frac{1}{4\pi} \times$  the limit of  $S$  for infinite condensation of  $z_1$  and  $z_2$ .

Let us on the other hand represent each pair of points consisting of a point of a chord of  $k_1$  and a point of a chord of  $k_2$ , by the endpoint of a vector with fixed origin  $O$ , and having the size and direction of the vector connecting the corresponding pair of points. Then for infinite condensation of  $z_1$  and  $z_2$  the ratio of the element of  $S$  corresponding to  $\alpha_1$  and  $\alpha_2$  to the value of the solid angle projecting out of  $O$  the parallelogram representing the chords  $\alpha_1$  and  $\alpha_2$ , approaches indefinitely to unity, and so does the ratio of the element of  $S$  corresponding to  $\alpha_1$  and  $\alpha_2$  to the part of  $B$  covered for the simplicial approximation<sup>1)</sup> of  $\alpha$  corresponding to  $z$ , by the "base parallelogram" resulting from  $\beta_1$  and  $\beta_2$ .

As farthermore on account of the rectifiability of  $k_1$  and  $k_2$  the sum of the absolute values of the elements of  $S$  for infinite condensation of  $z_1$  and  $z_2$  cannot exceed a certain finite value,  $\frac{S}{4\pi}$  converges indeed to the looping coefficient defined as the degree of the representation  $\alpha$ .

On the other hand for rectifiable curves holds also the definition of the looping coefficient as a variation of a solid angle mentioned in the beginning, and we easily see also this definition to be equivalent to the expression (1).

## § 2.

Let now in  $S\rho_n$  be given a two-sided closed  $h$ -dimensional space  $\varrho_1$  and a two-sided closed  $(n-h-1)$ -dimensional space  $\varrho_2$  not cutting  $\varrho_1$ , each provided with a positive indicatrix. We make  $\varrho_1$  as well

<sup>1)</sup> Mathem. Annalen 71, p. 102.

as  $\varrho_2$  measurable<sup>1)</sup>, and we consider the pairs of points consisting of a point of  $\varrho_1$  and a point of  $\varrho_2$ . A part of  $R$  determined by an element of  $\varrho_1$  and an element of  $\varrho_2$  we shall call a *paralleloelement*. It appears as a continuous one-one image of a  $(h, n-h-1)$ -*simplotope*<sup>2)</sup>. Let us call a division of a simplotope  $\pi$  into simplexes with one common vertex inside  $\pi$ , whilst the remaining vertices lie in the boundary of  $\pi$ , a "canonic division", then we can bring about such a canonic division by first executing it for the two-dimensional limits, then for each three-dimensional limit by projecting the divisions of its two-dimensional limits out of an arbitrary inner point, then for each four-dimensional limit by projecting the divisions of its three-dimensional limits out of an arbitrary inner point, and so on. Accordingly we can divide the paralleloelements of  $R$  into  $(n-1)$ -dimensional elements in such a way, that by their mode of being joined they cause  $R$  to appear as a *closed  $(n-1)$ -dimensional space*.

Let  $p$  be a paralleloelement of  $R$ ,  $d_1$  resp.  $d_2$  the corresponding element of  $\varrho_1$  resp.  $\varrho_2$ ,  $A_1 A'_1 \dots A_1^{(h)}$  a positive indicatrix of  $d_1$ ,  $A_2 A'_2 \dots A_2^{(n-h-1)}$  a positive indicatrix of  $d_2$ , we then define the row of pairs of points  $(A_1 A_2)$ ,  $(A'_1 A_2)$ ,  $\dots$ ,  $(A_1^{(h)} A_2)$ ,  $(A_1^{(h)} A'_2)$ ,  $\dots$ ,  $(A_1^{(h)} A_2^{(n-h-1)})$  as a positive indicatrix of the partitional simplex of  $p$  determined by those pairs of points, and with the aid of it we fix the positive indicatrix of the elements of  $R$  belonging to  $p$ . In this way we determine of all elements of  $R$  the positive indicatrix, where for two arbitrary elements having an  $(n-2)$ -dimensional limit in common these indicatrices satisfy the relation prescribed for *two-sided spaces*.

So  $R$  is a *closed two-sided  $(n-1)$ -dimensional space*.

The set of the vector directions of  $Sp_n$  forms likewise a closed two-sided  $(n-1)$ -dimensional space (of the connection of the  $(n-1)$ -dimensional sphere) which we shall represent by  $B$ . The positive indicatrix of the spheres of  $Sp_n$  (and with it at the same time the positive indicatrix of  $B$ ) we determine by regarding them as boundary of their inner domain.

If we conjugate to each pair of points consisting of a point of  $\varrho_1$  and a point of  $\varrho_2$  the direction of the vector connecting the two

<sup>1)</sup> *ibid.*, p. 98—100.

<sup>2)</sup> Let in  $Sp_{n-1}$  be given a plane  $h$ -dimensional space  $v$  and a plane  $(n-h-1)$ -dimensional space  $w$ . Let  $S_v$  be a simplex in  $v$ ,  $S_w$  a simplex in  $w$ . The set of those points of  $R_{n-1}$  which in the direction of  $w$  project themselves on  $v$  in  $S_v$ , and in the direction of  $v$  project themselves on  $w$  in  $S_w$ , form by definition an  $(h, n-h-1)$ -*simplotope*. Of a simplotope the limiting spaces of any number of dimensions are likewise simplotopes. (Comp. P. H. SCHOUTE, "Mehrdimensionale Geometrie", Vol. II, p. 45).

points, we determine a *continuous one-one representation*  $a$  of  $R$  on  $B$ . To this representation belongs a finite integer  $c$  independent of the mode of measurement of  $R$ , and therefore also of the mode of measurement of  $\varrho_1$  and  $\varrho_2$ , which is called the *degree* of the representation, and has the property that the image of  $R$  covers positively each partitional domain of  $B$  in toto  $c$  times.

It is this degree of representation which we define as the *looping coefficient of  $\varrho_1$  with respect to  $\varrho_2$* .

Exchange of  $\varrho_1$  and  $\varrho_2$  has only this consequence that the indicatrix of  $R$  changes its sign in some cases, and that each image point on  $B$  is replaced by its opposite point. *So the looping coefficient of  $\varrho_1$  with respect to  $\varrho_2$  and the looping coefficient of  $\varrho_2$  with respect to  $\varrho_1$  are either equal or opposite.*

We shall now show that if  $\varrho_1$  and  $\varrho_2$  are *evaluable*, i. e. if they have a definite finite  $h$ -dimensional resp.  $(n-h-1)$ -dimensional volume, the looping coefficient of  $\varrho_1$  with respect to  $\varrho_2$  can be expressed by the formula:

$$\frac{1}{k_n} \int \text{Vol. prod. } (di_1, di_2, r^{1-n}). \quad \dots \quad (2)$$

where  $k_n$  represents the  $(n-1)$ -dimensional volume of an  $(n-1)$ -dimensional sphere described with a radius 1 in the Euclidean  $Sp_n$ .

If namely  $\varrho_1$  and  $\varrho_2$  are evaluable, this integral can be interpreted as follows: We construct in  $\varrho_1$  resp.  $\varrho_2$  a simplicial division  $z_1$  resp.  $z_2$ . To this corresponds a simplicial division  $z$  of  $R$ , whose base simplexes are determined in connection with the base simplexes of  $\varrho_1$  and  $\varrho_2$  in the same way as we have determined above the elements of  $R$  in connection with the elements of  $\varrho_1$  and  $\varrho_2$ . Each base simplex of  $z_1$  resp.  $z_2$  we replace by the plane simplex with the same vertices. Let  $\alpha_1$  be the plane simplex corresponding to the base simplex  $\beta_1$  of  $\varrho_1$ ,  $\alpha_2$  the plane simplex corresponding to the base simplex  $\beta_2$  of  $\varrho_2$ ,  $r$  the distance of their centres of gravity, then  $\alpha_1$  and  $\alpha_2$ , the former regarded as an  $h$ -dimensional, the second as an  $(n-h-1)$ -dimensional vector, determine together with a linevector of size  $r^{1-n}$  in the direction of the straight line connecting their centres of gravity, a certain volume product<sup>1)</sup>. Of the volume

1) The sign of this volume product we determine as follows: After having formed in the manner described above out of  $(-1)^h \times$  the positive indicatrix of  $\alpha_1$  and the positive indicatrix of  $\alpha_2$  an indicatrix of a simplotope  $s$  parallel to  $\alpha_1$  and  $\alpha_2$ , we add to the latter indicatrix the endpoint of a linevector described out of a point of  $s$  in the direction of the straight line connecting the centres of gravity of  $\alpha_2$  and  $\alpha_1$ . The sign of the  $n$ -dimensional indicatrix found in this way determines the sign of our volume product.

products appearing in this way for the different pairs  $(z_1, z_2)$  we take the sum  $S$ , our integral is to be regarded as  $\frac{1}{k_n} \times$  the limit of  $S$  for infinite condensation of  $z_1$  and  $z_2$ .

Let us on the other hand represent each pair of points consisting of a point of a plane simplex determined by  $z_1$  and a point of a plane simplex determined by  $z_2$ , by the endpoint of a vector with fixed origin  $O$ , and having the size and direction of the vector connecting the corresponding pair of points. Then for infinite condensation of  $z_1$  and  $z_2$  the ratio of the element of  $S$  corresponding to  $z_1$  and  $z_2$  to the value of the solid angle projecting out of  $O$  the simplotope representing the simplexes  $z_1$  and  $z_2$ , approaches indefinitely to unity, and so does the ratio of the element of  $S$  corresponding to  $z_1$  and  $z_2$  to the part of  $B$ , filled for the simplicial approximation of  $\alpha$  corresponding to  $z$ , by the "base simplotope" resulting from  $\beta_1$  and  $\beta_2$ .

As farthermore on account of the evaluability of  $\varrho_1$  and  $\varrho_2$  the sum of the absolute values of the elements of  $S$  for infinite condensation of  $z_1$  and  $z_2$  cannot exceed a certain finite value,  $\frac{S}{k_n}$  converges indeed to the looping coefficient defined as the degree of the representation  $\alpha$ .

### § 3.

Let us now consider in  $Sp_n$  two sets of points  $\varrho'_1$  and  $\varrho'_2$  which have no point in common and are successively a continuous one-one image of an  $h$ -dimensional two-sided closed space  $\varrho_1$  and of an  $(n-h-1)$ -dimensional two-sided closed space  $\varrho_2$ , then for these all the considerations of the former § remain of force. Let farthermore  $\varrho_1''$  be a second continuous one-one image of  $\varrho_1$ , and let  $\varrho_2''$  be a second continuous one-one image of  $\varrho_2$ , then there exists a quantity  $\eta$  with the property that if the distance of two corresponding points of  $\varrho_1'$  and  $\varrho_1''$  as well as the distance of two corresponding points of  $\varrho_2'$  and  $\varrho_2''$  is smaller than  $\eta$ , the looping coefficient of  $\varrho_1''$  with respect to  $\varrho_2''$  is equal to the looping coefficient of  $\varrho_1'$  with respect to  $\varrho_2'$ .

From this ensues that in  $Sp_n$  the looping coefficient of an  $h$ -dimensional two-sided closed space  $\varrho_1$  with respect to an  $(n-h-1)$ -dimensional two-sided closed space  $\varrho_2$  not intersecting  $\varrho_1$  is equal to the value of the integral

$$\frac{1}{k_n} \int \text{Vol. prod. } (di_1, di_2, r^{1-n})$$

for an arbitrary *simplicial approximation*<sup>1)</sup>  $a(\varrho_1)$  of  $\varrho_1$  and an arbitrary simplicial approximation  $a(\varrho_2)$  of  $\varrho_2$ .

Let  $K_1$  and  $K_2$  be in  $S_{p_n}$  two spheres lying outside each other,  $a(\varrho_1)$  a simplicial image of  $\varrho_1$  lying inside  $K_1$ ,  $a(\varrho_2)$  a simplicial image of  $\varrho_2$  lying inside  $K_2$ . The looping coefficient of  $a(\varrho_1)$  with respect to  $a(\varrho_2)$  is then *zero*; for, by transferring  $K_2$  with  $a(\varrho_2)$  outside  $K_1$  to infinity, we can vary this looping coefficient only continuously, thus not at all.

We can now transform  $a(\varrho_2)$  continuously into  $a(\varrho_1)$  by causing the base points<sup>2)</sup> of  $a(\varrho_2)$  to describe continuous paths, and we can choose for these base point paths such broken lines that in none of the intermediary positions of  $a(\varrho_2)$  an  $(h-1)$ -dimensional element limit of  $a(\varrho_1)$  has a point in common with  $a(\varrho_2)$ , neither an  $(n-h-2)$ -dimensional element limit of  $a(\varrho_2)$  has a point in common with  $a(\varrho_1)$ , whilst those intermediary positions of  $a(\varrho_2)$  which correspond to the angles of the base point paths, have no point in common with  $a(\varrho_1)$ .

Then for this variation of  $a(\varrho_2)$  the looping coefficient of  $a(\varrho_1)$  with respect to  $a(\varrho_2)$  increases by a unit as often as an element  $e_1$  of  $a(\varrho_1)$  is traversed by an element  $\eta_2$  of  $a(\varrho_2)$  *positively*, i.e. in such a way that the volume product of  $e_1$ ,  $\eta_2$ , and the direction of motion of the traversing point is positive according to the above definition.

If on the other hand we understand by  $na(\varrho_2)$  resp.  $na(\varrho_1)$  a two-sided  $(n-h)$ -dimensional *net fragment*<sup>3)</sup>, limited by  $a(\varrho_2)$  resp.  $a(\varrho_1)$  and crossing  $a(\varrho_1)$  only in a finite number of points, belonging neither to an  $(h-1)$ -dimensional base limit of  $a(\varrho_1)$ , nor to an inner  $(n-h-1)$ -dimensional base limit of  $na(\varrho_2)$  resp.  $na(\varrho_1)$ , whilst such a crossing is called positive, if in the crossing point the  $n$ -dimensional indicatrix composed of  $(-1)^h \times$  the positive indicatrix of  $a(\varrho_1)$  and the positive indicatrix of  $na(\varrho_2)$  resp.  $na(\varrho_1)$  is positive, then for the above-mentioned variation of  $a(\varrho_2)$  the algebraical sum of the number of positive and the number of negative crossings of  $a(\varrho_1)$  and  $na(\varrho_2)$  increases likewise by a unit each time that  $a(\varrho_1)$  is traversed by  $a(\varrho_2)$  positively.

*From this ensues that the looping coefficient of  $\varrho_1$  with respect to  $\varrho_2$  can also be defined as the algebraical sum  $\omega\{a(\varrho_1), na(\varrho_2)\}$  of the number of positive and the number of negative crossings of an arbitrary simplicial approximation  $a(\varrho_1)$  of  $\varrho_1$  and an arbitrary  $(n-h)$ -dimen-*

1) Mathem. Annalen 71, p. 102 and p. 316.

2) *ibid.*, p. 317.

3) *ibid.*, p. 316.

sional net fragment  $na(\varrho_2)$ , limited by an arbitrary simplicial approximation  $a(\varrho_2)$  of  $\varrho_2$ .

That this algebraical sum is unequivocally determined by  $\varrho_1$  and  $\varrho_2$ , can also be shown by a direct proof.

If, namely, we have two different net fragments  $na(\varrho_2)$  and  $n'a(\varrho_2)$ , limited by the same simplicial approximation  $a(\varrho_2)$ , and if we represent the net fragment obtained out of  $n'a(\varrho_2)$  by inversion of the indicatrix, by  $n''a(\varrho_2)$ , then  $na(\varrho_2)$  and  $n''a(\varrho_2)$  form together a *two-sided closed net*<sup>1)</sup>, so that  $\omega\{a(\varrho_1), na(\varrho_2) + n''a(\varrho_2)\}$  must be equal to zero, thus  $\omega\{a(\varrho_1), n'a(\varrho_2)\} = \omega\{a(\varrho_1), na(\varrho_2)\}$ .

If furthermore we have two different simplicial approximations  $a(\varrho_1)$  and  $a'(\varrho_1)$  corresponding to one and the same mode of measurement of  $\varrho_1$ , two different simplicial approximations  $a(\varrho_2)$  and  $a'(\varrho_2)$  corresponding to one and the same mode of measurement of  $\varrho_2$ , and two two-sided net fragments  $na(\varrho_2)$  and  $na'(\varrho_2)$ , which, leaving their rims out of consideration, have the same base points, then for continuous transformation of  $a'(\varrho_1)$  into  $a(\varrho_1)$  we have:

$$\omega\{a'(\varrho_1), na(\varrho_2)\} = \omega\{a(\varrho_1), na(\varrho_2)\},$$

and for continuous transformation of  $a'(\varrho_2)$  into  $a(\varrho_2)$ :

$$\omega\{a'(\varrho_1), na'(\varrho_2)\} = \omega\{a'(\varrho_1), na(\varrho_2)\}.$$

If finally we have two different modes of measurement  $\mu_1$  and  $\mu'_1$  with corresponding indicatrices of  $\varrho_1$ , and two different modes of measurement  $\mu_2$  and  $\mu'_2$  with corresponding indicatrices of  $\varrho_2$ , then on account of the theorem, that a continuous one-one correspondence between two closed spaces possesses the degree  $\pm 1$ <sup>2)</sup>, there exists a simplicial approximation  $a'(\varrho_1)$  corresponding to  $\mu'_1$ , covering a simplicial approximation  $a(\varrho_1)$  corresponding to  $\mu_1$  with the degree *one*, and a simplicial approximation  $a'(\varrho_2)$  corresponding to  $\mu'_2$ , covering a simplicial approximation  $a(\varrho_2)$  corresponding to  $\mu_2$  with the degree *one*, from which ensues immediately:

$$\omega\{a'(\varrho_1), na'(\varrho_2)\} = \omega\{a(\varrho_1), na(\varrho_2)\},$$

with which the proof that the abovementioned algebraical sum depends exclusively on  $\varrho_1$  and  $\varrho_2$ , is completed.

In close connection with the looping coefficient is the notion of *enlaced spaces* recently introduced by LEBESGUE<sup>3)</sup>. Two spaces enlaced

1) *ibid.*, p. 316.

2) *ibid.*, p. 324 and p. 598.

3) C. R., 27 mars 1911.

according to LEBESGUE, possess in our terminology with respect to each other an *odd* looping coefficient. But to justify his definition LEBESGUE has neglected to prove that the being enlaced or not of two spaces is independent of the manner in which they are measured, which property is established only by the above reasonings.

The developments joined by LEBESGUE to his definition can meanwhile be made entirely rigorous by replacing the notion "*enlaced*" by: "*enlaced for a definite mode of measurement.*"



(June 25, 1912).



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING  
of Saturday June 29, 1912.

*President:* Prof. H. A. LORENTZ.

*Secretary:* Prof. P. ZEEMAN.

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**Microbiology.** — “*Mutation in Penicillium glaucum and Aspergillus niger under the action of known factors.*” By H. J. WATERMAN. (Communicated by Prof. M. W. BEIJERINCK).

(Communicated in the meeting of May 25, 1912).

A. *Penicillium glaucum.*

In solutions of *p*- and *m*-oxybenzoic acid a spontaneous growth of mould had developed at the air. From this material, which floated on the liquid, a pure culture of *Penicillium glaucum* was obtained by isolation on malt agar, which culture was used in the biochemical investigations described by Prof. BÖESEKEN and WATERMAN.<sup>1)</sup> It looked quite normally green and had the peculiar “mould smell”. The culture was transferred some times in the course of a year; mostly to protocatechetic acid, and a few times also to *p*-oxybenzoic acid as sole carbon food.

After about a year, white, jelly-like spots were observed in a great number of the films floating in ERLÉNMEIJER-flasks of 200 cc. Seen under the microscope these spots proved to have produced but few spores, whereas the mycelium and hyphae were normally developed. The phenomenon became still more prominent if considerable quantities of other substances retarding the growth, such as salicylic and trichloracrylic acid were added to the *p*-oxybenzoic acid.

TABLE I.

50 cc. tapwater, 0,05 % NH<sub>4</sub>Cl, 0,05 % KH<sub>2</sub>PO<sub>4</sub>, 0,02 % MgSO<sub>4</sub>; *t* = 20–21°.

Nr	Carbon compound added.	13 days after inoculation
1	0,15 gr. <i>p</i> -oxybenzoic acid (0,3 %)	Aspect rather normal, only slightly mucous.
2	” ” ” ”	
3	0,15 gr. <i>p</i> -oxybenzoic acid + 3,5	Very mucous, most in 5, least in 3. In 4 and especially in 5 few spores.
4	” ” ” ” + 7,3	
5	” ” ” ” + 12,2	
6	0,15 gr. <i>p</i> -oxybenzoic acid + 3,4	6, 7, 8 successively like 3, 4 and 5, but the phenomenon less marked. <sup>2)</sup>
7	” ” ” ” + 7,1	
8	” ” ” ” + 14	

1) BÖESEKEN and WATERMAN. These Proceedings Vol. 14, p: 604, 608, 928, 1112.

2) Salicylic acid retards the growth more than trichloracrylic acid.

It was supposed that the observed alteration in the mould film might be explained by mutation, which was proved true by the biological method. By isolation on malt gelatin two forms could be obtained from these cultures. One of these was very lightly coloured in consequence of the small number of spores. This form will be indicated as "the mutant". The other had preserved the dark green colour and had evidently remained identic with the original culture. The difference between the two forms was very marked.

So it cannot be doubted, that at prolonged cultivation in presence of *p*-oxybenzoic acid mutation does indeed take place. With protocatechetic acid as carbon food the same was observed. Furthermore, Table I shows that salicylic acid and trichloroacrylic acid promote this process.

In the floating mould layer the extent of the mutant was greatest in those flasks where the said antiseptica were most concentrated.

At a continued cultivation on malt agar the thus obtained mutant, which in all the said cases seemed the same, remained constant.

If the mutant and the original form were again transferred to a *p*-oxybenzoic acid solution with the anorganic food named in the table, they also preserved their properties.

Under the microscope the mutant produced considerably fewer spores than the primitive form<sup>1)</sup> and its mycelium had a greater tenacity, which was repeatedly stated.

There was besides a peculiar difference in smell, as the original form gave out the well-known "mould odour", which the mutant did not.

The growth of the mutant on para-oxybenzoic acid was considerably slower than that of the primitive form.

In the laboratory a third form of *Penicillium glaucum* was present, distinguished from the original form of my experiments by darker green spores and which served for the subsequent experiments.

It was first cultivated during four days on *p*-oxybenzoic acid where the growth was very slow; it was then transferred to a new flask with the same medium, and now the growth was much accelerated, which proved that in these few days accommodation to the para-oxybenzoic acid had taken place. Furthermore it was observed that also here, after a prolonged cultivation on *p*-oxybenzoic acid mutation occurred. Substances such as tetrachlor-propionamid  $\left( \begin{array}{c} \text{CHCl}_2\text{CCl}_2\text{C}=\text{O} \\ \backslash \text{NH}_2 \end{array} \right)$  and pentachlor-propionamid  $\left( \begin{array}{c} \text{CCl}_3-\text{CCl}_2-\text{C}=\text{O} \\ \backslash \text{NH}_2 \end{array} \right)$ ,

<sup>1)</sup> Whether the difference in the number of spores was accompanied by a difference in intensity of colour is not settled as yet.

likewise compounds which retard the growth, again favoured the mutation, so that this process seems rather general.

The smaller number of spores and the less rapid growth evidently lead to explain the properties of this mutant by a loss of characteristics or gens.<sup>1)</sup>

### B. *Aspergillus niger*.

We started for this investigation from a pure culture of the laboratory collection, which was first cultivated some time on a 2% succinic acid solution. In several inoculations in ERLÉNMEIJER-flasks with different culture media, a considerable alteration of this black mould occurred.

Using a 2% solution of galactose it was observed that in this medium, beside the primitive form with black spores, a brown and a white one appeared, which three forms may be called I, II, and III.

On a 2% rhamnose solution of for the rest the same composition (tapwater, 0,05% NH<sub>4</sub>Cl, 0,05% KH<sub>2</sub>PO<sub>4</sub>, 0,02% MgSO<sub>4</sub>) the black and the brown forms (I) and (II) were distinctly present, the white form (III) wanting. A tube, to which beside the food consisting of 0.3% *p*-oxybenzoic acid, 9 mgr. (per 50 c.c.) dichloracrylic acid  $\left( \begin{array}{c} \text{CH}=\text{CCl}-\text{C}=\text{O} \\ \text{Cl} \qquad \qquad \backslash \text{OH} \end{array} \right)$  had been added, showed after about a month a quite brown mould layer. Later experiments proved that in nutrient solutions with 2% glucose as source of carbon, under the influence of 1% boric acid likewise mutation occurs.

The three forms from the galactose solution were isolated on malt agar; II and III distinctly gave fewer spores than I, and III fewer than II. They were transferred to media of tapwater-agar to which beside 0,05% NH<sub>4</sub>NO<sub>3</sub> and 0,05% KH<sub>2</sub>PO<sub>4</sub>, 2% galactose was added. On this plate the appearance of the mutants was different from that on the malt agar. From this galactose plate I, II, and III were again transferred to malt agar; the latter cultures were used for the examination of the plastic equivalent of the carbon, whereunto we return below.

It was clear under the microscope that besides a smaller quantity of spores, there was also a decrease of colour intensity of these spores in II and III, which had become brown instead of black. The question whether III might also be obtained without any spores

<sup>1)</sup> Compare M. W. BEIJERINCK, Mutation bei Mikroben. Folia Microbiologica, 1912, p. 5.

at all must be answered negatively, as is shown by the subsequent experiments.

By starting every time from a single spore, cultures were obtained which remained identic to the material used for the sowing. If the mycelium, carefully separated from the spores was separately sown, no difference appeared between the product obtained from it and that from the spores.

Possibly form II is the same as the brown form obtained some months ago by FRL. SCHIEMANN <sup>1)</sup> under the action of kaliumbichromate.

In earlier experiments on the metabolism of *Aspergillus niger* irregularities had been found, which then could not be accounted for, but which can now be explained by the observed mutations. In the said experiments it was determined what percentage of the assimilated quantity of carbon was at a given moment bound in the body of the mould and what percentage was excreted as carbonic acid by respiration or otherwise. The first percentage may be called "*plastic aequivalent*" of the carbon, in accordance with the term used in researches on the luminous bacteria by Professor BEIJERINCK <sup>2)</sup> whereas the percentage of the carbon which at a given moment is respired will be called "*respiration aequivalent*".

On a 0,3 % paraoxybenzoic acid solution (anorg. food: tapwater, 0,05 % NH<sub>4</sub>Cl, 0,05 % KH<sub>2</sub>PO<sub>4</sub>, 0,02 % MgSO<sub>4</sub>; t = 32–33°C.) was found after 45 days a plastic aequivalent of the carbon of 34 %. In other cultures likewise on para-oxybenzoic acid and obtained by inoculation with the said culture, whose plastic aequivalent was 34 %, this number amounted after 27–28 days respectively to 20 and 16 %.

As this lowering of the plastic aequivalent under the influence of the *p*-oxybenzoic acid might possibly be ascribed to the above mentioned mutation the question arose: Do forms I, II, and III quantitatively differ considerably in their metabolism?

The experiments resumed in Table II prove that this is really the case.

The differences are, as we see, enormous and they sufficiently explain the described irregularities.

By this method we are thus enabled to conclude to mutation even then when visible external differences between the cultures are wanting.

Likewise as for the mutation of *Penicillium glaucum* we see in

<sup>1)</sup> Ber. d. Deutsch. Bot. Gesell. 1912 Heft 2, 28 März.

<sup>2)</sup> Aliment photogène et plastique. Archives Néerlandaises, T. 24, p. 1 1891.

TABLE II.

200 cc. ERLIENMEIJER-flasks of Jenaglass with 50 cc. tapwater, in which 0.05 %  $\text{NH}_4\text{Cl}$ , 0.05 %  $\text{KH}_2\text{PO}_4$ , 0.02 %  $\text{MgSO}_4$  and 150 mgr. para-oxybenzoic acid, temperature about  $32^\circ-33^\circ$ .

	Form I	Form II	Form III
Plastic aequivalent of the carbon in two experiments	29 % <sub>0</sub>	18 % <sub>0</sub>	15 % <sub>0</sub>
	28 % <sub>0</sub>	18 % <sub>0</sub>	16 % <sub>0</sub>

the here described mutation a loss of characteristics or gens, for beside the loss in colour intensity we stated a decrease in the number of spores.

On the other hand it was observed, that the new forms were distinguished from the primitive one by a much more vigorous combustion of the *p*-oxybenzoic acid to carbonic acid, their "respiration aequivalent" being found to amount from 71—72 % in I, to 82 % in II, and even to 85 % in III.

If, as in the case observed, all other carbon-containing secondary products are wanting, the sum of the two aequivalents is of course = 100.

The here introduced aequivalents only relate to the *element carbon*, whereas the hitherto used coefficients refer to the number of grams of dry substance, to the number of grams of assimilated carbon, or to the carbonic acid evolved during the life of the related organism <sup>1)</sup>.

The here introduced aequivalents are to be preferred to the other terms referred to, because the chemical composition of the food, of the constituents of the organism, and of the carbonic acid are so widely divergent.

Finally I bring my thanks to Mr H. C. JACOBSEN, assistant to the Laboratory for Microbiology, for his kind help in these experiments.

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<sup>1)</sup> See for instance: KUNSTMANN, Ueber das Verhältniß zwischen Pilzernte und verbrauchter Nahrung. Dissertation Leipzig, 1895. Also: NATHANSOHN, Stoffwechsel der Pflanzen, 1910.

**Anatomy.** — “*On the external nose of Primates*”. By G. P. FRETZ.  
(Communicated by Prof. Dr. L. BOLK).

The distinction of monkeys into Platyrrhini and Catarrhini is of ancient date and generally adopted. It seems to be little known by whom this distinction has first been made, in the systematical works at least the name is not mentioned. The object of the present communication is to premise the description of this classification, as it has been given by BUFFON and E. GEOFFROY ST. HILAIRE and amended by Is. GEOFFROY ST. HILAIRE, and to test by this formulization the result of an investigation I have made.

About 1765 BUFFON was the first to use the external nose as a systematic characteristic for the classification of monkeys, which coincides with their geographical dispersion over the two continents<sup>1)</sup>. He writes:<sup>2)</sup> “les singes de l’ancien continent ont la cloison des narines étroite, et ces mêmes narines sont ouvertes au-dessous du nez comme celles de l’homme” and “les singes du nouveau monde ont tous la cloison des narines fort épaisse, les narines ouvertes sur les côtés du nez et non pas en dessous.”

In 1812 ET. GEOFFROY ST. HILAIRE<sup>3)</sup> divides the monkeys in his *Tableau des Quadrumanes* into catarrhinins, catharrini or monkeys of the Old World and platyrrhinins, plathyrrhini or American monkeys. He borrows BUFFON’S description and adds to it, that with catarrhine monkeys the nose-bones dissolve before the shedding of the teeth (p. 86) whilst with platyrrhines the suture between these bones disappears only at a later age. Later French authors sometimes bring out still more distinctly that the characteristic has been derived from the external nose. So DESMAREST<sup>4)</sup> writes: “les singes catarrhinins ou singes de l’ancien monde (ont les) narines rapprochées l’une de l’autre” and “les singes platyrrhinins ou singes du nouveau continent (ont les) narines écartées l’une de l’autre”. In the same way G. CUVIER (ed. 1829 I p. 99) F. CUVIER<sup>5)</sup>, DE BLAINVILLE<sup>6)</sup>, P. GEVAIS<sup>7)</sup>, BROCAC<sup>8)</sup>.

1) Compare Is. G. ST. HILAIRE, *Mém. du Muséum*, T. 17, p. 129; 1828.

2) BUFFON, *Oeuvres complètes*; ed. 1837 IV, 2, p. 687, 1,

3) E. G. ST. HILAIRE, *Annales du Muséum*, T. 19, 1812.

4) DESMAREST, *Mammologie* 1, Partie, p. 30, Paris.

5) G. ST. HILAIRE et F. CUVIER, *Hist. Nat. des Mammifères*, T. 1, Paris 1824.

6) DE BLAINVILLE, *Ostéographie des Mammifères*, T. 1, p. 6, Paris 1839—64.

7) P. GERVAIS, *Hist. nat. des Mammifères*, p. 8 and p. 113, Paris 1854.

8) BROCAC, *L’Ordre des Primates*, *Mém. d’Anthropologie*, T. III, p. 11, 1877.

Likewise SCHLEGEL<sup>1)</sup>. Less exact descriptions are given by GIEBEL<sup>2)</sup>, CLAUS<sup>3)</sup>, and M. WEBER<sup>4)</sup>.

In order to preclude incorrect representations, it is necessary to premise that the classification of monkeys into Catarrhini and Platyrrhini is based on external distinctive features namely on the distance and the location of the nostrils. Catarrhini or monkeys of the Old World are monkeys with small *distantia internarina* and nostrils turned downward, Platyrrhini or monkeys of the New World have a large *distantia internarina* and nostrils turned sideways.

ISIDORE GEOFFROY ST. HILAIRE<sup>5)</sup> takes the classification of BUFFON and of his father as point of issue for his investigations. He comes however to the conclusion that the distinction of monkeys according to their external nose, without more, does not coincide with their geographical dispersion over the two continents. According to him *Eriodes*, *Lagothrix* and *Nyctipithecus*, all of them American monkeys, agree, with regard to their nostrils, almost entirely with the monkeys of the Old World; on the other hand *Semnopithecus* and especially *Miopithecus* come very near up to the monkeys of the New World. IS. G. ST. HILAIRE therefore proposes the following compromise: "Il est permis de conserver à ces caractères toute leur généralité, à la condition d'en modifier l'expression, la cloison internasale étant toujours mince ou médiocrement épaisse *jamais large* chez les Singes de l'Ancien Monde, à quelque tribu qu'ils appartiennent; large ou médiocrement épaisse, *jamais mince* chez les Singes américains.

I have controlled this view by a great number of individuals. In my opinion it is not correct; when examining many monkeys, we see that the external nose of Platyrrhini with "la cloison internasale médiocrement épaisse" can always be distinguished from Catarrhini with a similar *distantia internarina*. It is true that it is difficult to express this difference in a single sentence.

Let us first pass under review the shape of the external nose of typical representatives of the two groups. The different species of *Cebus* have all a large *distantia internarina* and nostrils turned sideways; between these lies a superficial fossa *internarina*. The nostrils are rather wide oval, the oral part is the wider; from above and medial the processus *naviculares* of the maxilloturbinale penetrate

1) H. SCHLEGEL, Muséum d'Histoire naturelle, p. 3 and 4, Leyden 1876.

2) GIEBEL, Die Säugetiere, 1859, S. 1025.

3) CLAUS, Lehrbuch der Zoologie, 3 Aufl. II, S. 1199, 1876.

4) M. WEBER, Die Säugetiere, Jena 1904, p. 771 and 776.

5) IS. G. ST. HILAIRE, Extr. d'Archives du Muséum d'Hist. nat. T. 2, p. 6 and p. 39, Paris.



into them. Consequently the opening of the nose is kidney-shaped, with the convexity to the outside. The cartilaginous nose consists of the two cartilagine alares and the cartilago triangularis. The cartilago alaris is a rather broad, shell-shaped cartilage blade, surrounding the nostril at the top, medially and orally. The dorsal, lateral angle of the cartilago alaris is continued in the processus navicularis. If we prepare the median parietis of the cartt. alares separately and spread them out, we can follow the downward extremity of the cartilago triangularis that is continued in the foremost edge of the septum. The septum does not protrude free from between the cartt. alares. The proportions of *Chrysothrix* and *Hapale* are exactly like those of *Cebus*.

The form and composition of the cartilaginous nose of *Platyrrhini* can easily be derived from its form in the embryo. There it is the uninterrupted continuation of the internal nose, its frontal termination. The septum is gradually transformed into two cartilaginous blades, which at the top medially and orally limit the nostrils. In older foetal stages both the cartt. alares and the cartilago triangularis take their origin from these blades.

The slight prominence of the nose of *Platyrrhini* (*DESMAREST*) is caused by a slight protuberance of the region of each nostril separately. By their boundary the nostrils are more independent and wider open than those of *Catarrhines*; the cartt. alares are thicker. There is a sharp oral boundary of the nostril with regard to the upper-lip.

The external nose of *Catharrini*, as e.g. of *Macacus*, *M. sinicus*, *M. rhesus* is characterized by a small *distantia internarina* and downward directed nostrils. Instead of a *fossa internarina* a *sulcus interalaris* is often found here. The nostrils are in the direction of the lips not separated from these. They lie at the distal end of the cartt. alares and are enclosed by the latter only medially and not at the inferior side; therefore there is, between the two nostrils, a free duplicature of the skin, a *septum mobile*, that extends more or less on the upper-lip and forms here a slight protuberance. In the *septum mobile* a projecting part of the cartilago alaris, *crus mediale*, extends; I found this likewise in microscopic preparations of the full-grown nose. The region of the cartt. alares is often a little arched, as if it were inflated. The nostrils are narrow oval and long, the two rims almost touch each other, also on account of the thinness and flabbiness of the cartt. alares. Medially the beginning of the *processus navicularis* arches into the opening of the nose from the *maxilloturbinale*, which originates from the upper part of the cartt. alares. The cartt. alares are narrower and less curved than those of *Platyrrhini*; they run pretty well parallel. The *sulcus suprasedalis*

terminates in the cartilago triangularis. If one prepares the cartt. alares separately, and spreads them out, one sees that the cartilago triangularis extends between them as front edge of the septum nasi and protrudes a little to the front. Cercopithecids of which I examined several specimens are of exactly the same structure as these described Macacus.

If now types with a distantia internarina "mediocrement épaisse" are compared with these two types, one sees that the American monkey always represents the platyrrhine type, the monkey of the Old World always the catyrrhine type. Is. GEOFFROY ST. HILAIRE mentions *Semnopithecus* and *Miopithecus* (talapoin) as monkeys of the Old World with a rather large distantia internarina. In *Semnopithecus* namely in a specimen of *Lophopithecus melalophos* (s. *Semnophitecus melalophos*) I found the greatest distantia internarina of monkeys of the Old World. In the mentioned *Lophopithecus* this distance was 0.6 cm., over against 0.55 cm. in an *Ateles*, to be mentioned by-and-by. Yet one recognizes by the prominence of the whole nose, by the absence of the separation of the nostrils with regard to the upper-lip, by their regular narrow oval shape, the catarrhine nose. On the other hand the nose of an examined *Ateles grisescens* with a distantia internarina of 0.55 cm., with the sharply limited nostrils opening spontaneously indicates the platyrrhine monkey. The physiognomy of *Nyctipithecus trivirgatus*, likewise mentioned by Is. GEOFFROY ST. HILAIRE, is greatly different from that of the other Platyrrhini. The animal has a prominent nose and nostrils directed downward and sideways. A fossa internarina lies on the inferior part of the nose. The distance between the upper part of the nose and the rim of the upperlip is short. The nostrils have for the rest the sharp limitation of Platyrrhini.

With the prepared nose the distinction of the two forms is also always possible. With *Semnopithecus* the nostrils do not lie — as with *Macacus* — any longer on the oral but on the lateral extremity of the cartt. alares, they are however not enclosed in a labial direction, but a little crus mediale extends into the septum mobile. The cartilago alaris of Platyrrhini is stronger and more curved than that of Catarrhini.

The shape of the nose in the different tribes of Platyrrhini is little divergent. Only *Nyctipithecus* forms an exception. With *Ateles* the distantia internarina seems to vary considerably. So Is. G. ST. HILAIRE mentions *Lagothrix Humboldti*, belonging to the same family, as a specimen with rather small distantia internarina; it was not the case with the specimen that I examined. Of Catarrhini some species

have a more or less one-sidedly specialized nose. So with *Cynocephalis* (*C. porcarius*, *hamadryas*, *sphinx*, *mormon*) the nostrils are to the front, they lie at the oral extremity of the cartt. alares; these have a crus mediale. A detailed description of *Semnopithecus nasicus* has been given by WIEDERSHEIM<sup>1</sup>). With *Colobus* (*Cursinus*, *C. Pennanti*, *C. Kirikii*) the prominent part of the medial rim of the nostril, which extends inwardly into the processus navicularis of the maxilloturbinale, is strongly developed; the nose is flabby, the medial rim covers almost the nose-opening. With a *Colobus ursinus* the distantia internarina was "rather large", 0.55 cm. Of Catarrhini the external nose of *Semnopithecus* is least differentiated.

With *Cebus* the distantia internarina varies between 1,2 and 1,4 cm.; with *Ateles* between 0,55 (*Ateles grisescens*) and 1,15 cm.; with *Macacus* between 0,15 and 0,3 (1 specimen 0,4) cm.; with *Cercopithecus* between 0,3 and 0,4 cm.; with *Semnopithecus* between 0,3 and 0,55 (*Lophopithecus melanophos* 0,6 cm.).

Anthropoides are catarrhini like man. In the opening of the nose no Processus navicularis protrudes. *Hylobates* has entirely the nose of Catarrhini. The form of the nostrils is lengthened oval, the medial side however regularly curved; as no processus navicularis penetrates into the opening of the nose; the nostrils are not limited with regard to the upperlip. The flabby cartt. alares possess a crus mediale, which extends into the septum mobile. In two young specimens of *Simia satyrus* I found in the angle cartilago triangularis a small cartilaginous piece, a cartilago sesamoidea (of the human anatomy). There is here a vestige of a wing of the nose, the latter does not contain any cartilage. The oval nostrils lie in the plane of the face. The external nose of a specimen of a new born human being which I examined, agrees very much with that of a young Chimpanzee; in the latter the nostrils are likewise turned somewhat downward and to the front. In the new-born and young human beings the cartilago alaris extends still very regularly into the crus mediale. Only in the full-grown individual the crus mediale passes with a sharp deflection, angulus pinnalis, into the remaining part of the cart. alaris, crus laterale. Cartt. alares minores lie in the lateral continuation of the cartilago alaris (major). The wing of the nose does not contain any cartilage. Cartt. sesamoideae lie as with Orang between cart. alaris and cart. triangularis.

For Is. GEOFFROY ST. HILAIRE the result of his comparative examination — consequently his conclusion, that the gulf between Catar-

<sup>1</sup>) Zeitschr. f. Morph. und Anthropol. Bd. III S. 300.

rhini and Platyrrhini was almost entirely bridged over both by some Catarrhini and some Platyrrhini with a middling distantia inter-narina — was a support for his transformistical conception of the natural development. This was incorrect, as, I suppose, I have shown: the external nose of the monkeys of the Old World always differs from the nose of those of the New World. This fact can be connected with a supposed common descent, if we admit that in a mutation period of the ancestors, the two forms of the nose came into existence.

**Anatomy.** — “*On the Jacobson’s organ of Primates*”. By G. P. FRETZ. (Communicated by Prof. Dr. L. BOLK).

When examining older stages of development of some platyrrhine monkeys, *Chrysothrix*, *Cebus*, *Ateles*(?) and *Mycetes* I always found a well developed Jacobson’s organ. In some of these foetuses I ascertained the innervation by olfactoriusfibres. In embryos of 40 mm. of *Macacus cynomolgus* and *Semnopithecus maurus* no Jacobson’s organ is extant, but a well-developed basal cartilage, of which the Jacobson’s cartilage forms a part. Very young embryos of catarrhine monkeys have always a Jacobson’s organ. I made microscopic sections through the regions of the nose of two fullgrown specimens of *Cebus hypoleucus*. A well developed Jacobson’s organ was extant<sup>1)</sup> (Fig. 1). It terminates in the ductus nasopalatinus. A nerve-bundle (Fig. 1 *n. J. o*) is in connection with the mucous membrane. I ascertained in series of older embryos, as I said before, that the nerve for the Jacobson’s organ belongs to the olfactorius, and consequently I am of opinion that I may admit, that the nerve found in the full-grown animal is an olfactorius-bundle. The nerve nasopalatinus of the second branch of the trigeminus runs through the canalis nasopalatinus and in a groove between the processus palatinus of the maxilla and the lateral part of the Jacobson’s cartilage (Fig. 1, *n. np.*). A lamina praeductalis can be distinguished at the basal cartilage — before the ductus nasopalatinus —, continuations of which extend to the interior and to the front. The continuation to the interior and medially is the Jacobson’s cartilage.

Of Catarrhini I examined microscopic sections of the nasal region of a young *Macacus rhesus* and a *Semnopithecus entellus*. In both I find a well developed basal cartilage; the Jacobson’s organ however is missing. In *Macacus rhesus*, of which I examined a hardly interrupted series, a groove separates itself on both sides of the ductus

<sup>1)</sup> HERZFELD found a Jacobson’s organ in Hapale.

nasopalatinus, which can be followed to a distance of 36 sections of  $25 \mu$ . and lies nearly on the spot of the entrance of the Jacobson's

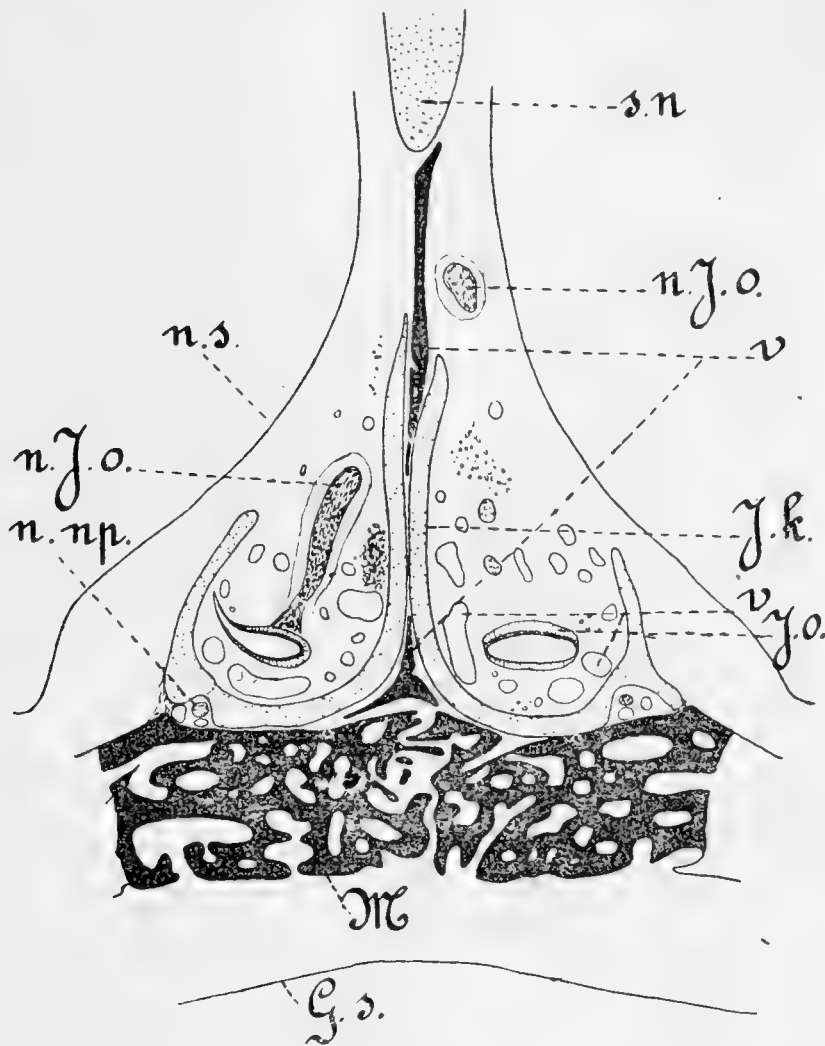


Fig. 1.

*Cebus hypoleucus*. Full-grown. Enlarged  $25 \times \frac{2}{3}$ . *J. o.* = Jacobson's organ; *n. J. o.* = nerve for the organ; *J. k.* = Jacobson's cartilage; *n. np.* = Nerv. nasopalatinus; *S. n.* = Septum nasi; *n. s.* = mucous membrane of the medial parietis of the nose-cavity; *g. s.* = mucous membrane of the palate  
*V* = Vomer; *m* = maxilla; *V* = Veins.

organ into the ductus nasopalatinus of Platyrrhini. This groove may be a rudiment of the Jacobson's organ; in embryos of Catarrhines with young cartilage skeleton however, the Jacobson's organ, which is then still extant, lies more dorsal.

All the mentioned foetuses of Platyrrhini possess likewise a small *lamina terminalis* dividing the hindmost part of the nose-cavity into a reduced regio olfactoria and a regio respiratoria.

The lamina terminalis is found in all mammals with a well developed olfactoria organ. It separates in the hindmost part of the nose-cavity from its lateral parietis, divides the nose-cavity into two parts situated the one above the other, and fuses with the vomer.

The independent regio olfactoria, formed in this way, which contains the olfactoria-conchae, terminates at the end blind against the frontal part of the praesphenoid.

In an almost fullgrown specimen of *Ateles ater* I found likewise an independent regio olfactoria, half a centimeter deep; it is also extant both in a museum-preparation of *Cebus fatuellus* (Fig. 2) and in a specimen of *Hapale jacchus* which I prepared myself.

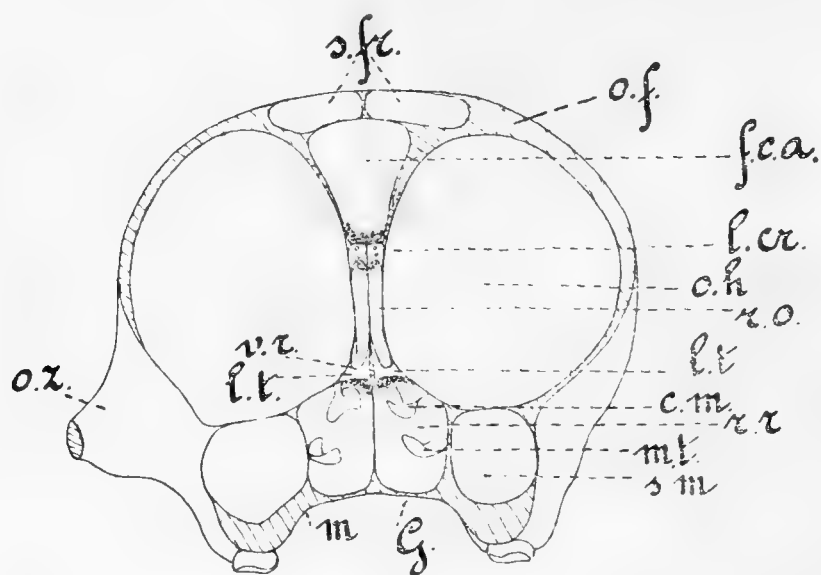


Fig. 2.

*Cebus fatuellus*. Museum-preparation 1906. N. 3. Frontal dish from the hindmost part of the nose-cavity, seen from behind. Enlarged  $\frac{3}{2} \times \frac{3}{4}$ .  
*l. cr.* = lamina cribrosa; *G* = palata; *lt* = lamina terminalis; *v. r.* = its free rim to the front; *r. o.* = regio olfactoria; *r. r.* = regio respiratoria; *mt* = maxilloturbinale; *c. m.* = concha media; *f. c. a.* = fossa cerebri anterior; *s. fr.* = sinus frontalis, *s. m.* = sinus maxillaris; *o. f.* = os frontale; *o. z.* = os zygomaticum; *m* = maxilla.

Among Catarrhini embryos of *Semnopithecus* do not show a vestige of lamina terminalis. Neither does an embryo of 47 mm. of *Macacus cynomolgus* do so; in younger *Macacus*-embryos I found sometimes a very little independent regio olfactoria. Nor has a young specimen of *Semnopithecus entellus* a vestige of lamina terminalis; a young animal with a shedding dental system of *Macacus sinicus* possesses on the frontal parietis of the praesphenoid a little protuberance; a last remainder of the lamina terminalis.

So we see, that in Platyrrhini a Jacobson's organ is extant and a reduced independent regio olfactoria, whilst in Catarrhines both are missing. Consequently the question presents itself whether this fact can give any information about the signification of the Jacobson's organ. By cauterisation of the organ of a cat and

some rabbits v. MIHALCOVICS<sup>1)</sup> has tried to discover the function; the animals continued to live in the same way. Here, with the monkeys, nature has made the experiment: Platyrrhini have a Jacobson's organ, Catarrhini miss it. No communication is known to me that, e. g. in taking their food, Platyrrhini behave differently from Catarrhini. In the latter a compensation-apparatus for the missing Jacobson's organ might exist. The hypothesis about the signification of the Jacobson's organ, most generally defended, is that it might be of use as a smelling organ in the mouth by tasting food (vide e. g. WEBER<sup>2)</sup> p. 153). If this hypothesis were correct, it would be possible to indicate in Catarrhini the compensation apparatus. In makrosmatical mammals the regio olfactoria is separated from the regio respiratoria by the lamina terminalis. This is not the case with Catarrhini; here the cavity of the mouth is in much better connection with the olfactory region by means of the lamina terminalis, consequently a separate organ of smell communicating with the mouth cavity through the canales incisivi is not so much required, and therefore the loss of the Jacobson's organ might be compensated by the disappearance of the secluded independent regio olfactoria.

HERZFELD<sup>3)</sup> however communicates a fact which is very unfavourable to the above mentioned hypothesis. According to this author horse, ass, giraffe, and camel possess a Jacobson's organ, but no ductus incisivus communicating with the mouth-cavity. It is likewise known, that among Chiropteres the Jacobson's organ is often missing, — this holds e. g. for *Pteropus* (HERZFELD, ZUCKERKANDL<sup>4)</sup> — whilst the preparation of this animal shows that it possesses a capacious independent regio olfactoria.

In virtue of these facts I am of opinion that in the simultaneous disappearance of the Jacobson's organ and the independent regio olfactoria in Catarrhini, and the continued existence of both in a reduced form in Platyrrhini, we must see a parallel phenomenon, an indication of the general reduction of the olfactory organ.

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1) V. v. MIHALCOVICS. Anatomische Hefte. XI Band, S. 78, 1898.

2) M. WEBER. Die Säugetiere, 1904.

3) P. HERZFELD, Zoologische Jahrbücher, 3 Bd., S. 551.

4) E. ZUCKERKANDL. Sitzungsberichte. Wien. Bd. 117. Math. phys. Cl.

**Physics.** — “*The magneto-optic KERR-effect in ferromagnetic compounds and metals.*” III. By PIERRE MARTIN of Geneva. (Communication from the BOSSCHA-Laboratory). (Communicated by Prof. H. DU BOIS).

The purpose of the following work was the extension of the investigations of LORIA <sup>1)</sup> on the magneto-optical properties of the newly obtained ferromagnetic compounds and alloys. I limited myself to the determination of the dispersion of different manganese and iron compounds, and to a repetition of the measurements for the case of the three chief metals. The literature has been fully discussed by LORIA so that it is not necessary to introduce it here; his experimental arrangement has been again adopted, for a description of which I may therefore refer to his publication. The direct vision monochromator, with high illuminating power, was subjected to a new calibration. Throughout, pole end-pieces (V) with rectangular bore were used, the profile of which ( $2,5 \times 4$  mm.) was nearly always exceeded by the size of the mirrors: the latter were irregularly shaped and fixed by means of plaster of Paris.

As a simple relation between the optical constants and the dispersion curve was sought for in vain by LORIA, I have not on this occasion determined the former. In general, for my specimens the extinction was good and consequently the ellipticity only very slight; considering the very small rotations in most cases, its determination appeared as yet scarcely possible of execution although certainly to be desired.

#### MATERIALS INVESTIGATED.

*Manganese compounds.* “Mn 65, Sn 35” =  $Mn_4Sn$ , and “Mn 35, Sb 65” =  $MnSb$  nearly, were very kindly given to me for investigation by Prof. TAMMANN. The relations between the amounts of the metals combined together correspond, according to HONDA, to the most ferromagnetic compound or alloy respectively <sup>2)</sup>. Besides these, I investigated a specimen of  $MnSb$  and  $MnB$  from Prof. WEDEKIND and also  $MnBi$  from Dr. HILPERT. The metal manganese was found inactive by LORIA.

*Iron compounds.* A piece of a carbon alloy consisting substantially of cementite ( $Fe_3C$ ) was kindly prepared for me by Dr. HILPERT. For normal pyrrhotine ( $Fe_7S_8$ ) I am indebted to Prof. P. WEISS of Zürich. In addition to these compact magnetic pyrite and amorphous

<sup>1)</sup> STANISLAW LORIA. These Proceedings Vol. 12, p. 835 and Vol. 14, p. 970.

<sup>2)</sup> KŌTARŌ HONDA. Ann. der Phys. 32, p. 1003, 1910.



iron sulphide from the laboratory collection were investigated. A piece of cerium-iron was also subjected to observation.

*Metals.* For electrolytic iron and also for pure cobalt and nickel I am again indebted to Prof. WEISS<sup>1)</sup>, who has investigated their saturation values of magnetisation.

The dispersion of the KERR-effect in the metals has been moreover previously determined by DU BOIS<sup>2)</sup>.

I beg here to express my best thanks to those gentlemen who have assisted me by supplying the materials.

In the following tables are given:  $\lambda$ , the wave-length of the observed light in  $\mu\mu$ .  $\Delta$ , the double rotation as observed in mm. on the scale after reversal of the current.  $\varepsilon$ , the simple rotation in minutes,  $\pm \sigma\varepsilon$ , the mean error in minutes and percent respectively.  $N$  the number of readings taken for each direction of the current.

#### MANGANESE COMPOUNDS.

*Manganese boride*<sup>3)</sup> (Mn B). In this case, my attempts to observe any rotation gave but negative results. Although the material was porous and on that account the mirror not very bright I was able to convince myself that if a rotation existed it was less than 0,3'.

*Manganese-tin.* (Mn 65, Sn 35 = Mn<sub>4</sub>Sn). The dispersion curve here remains entirely in the region of negative values (Fig. 1). The

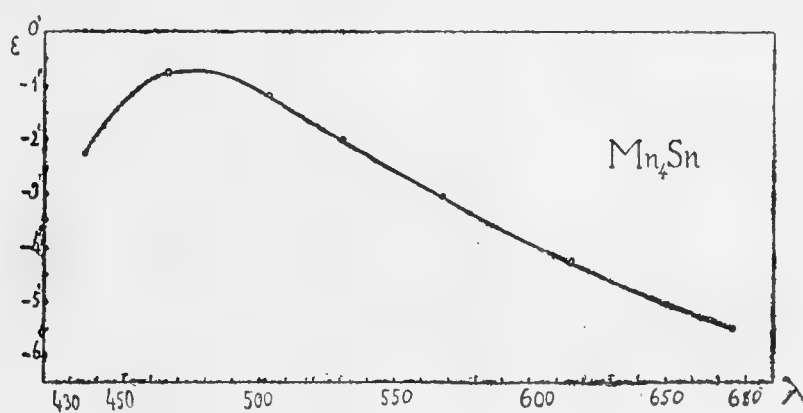


Fig. 1.

curve, which in the violet falls rather steeply, reaches a numerical minimum in the blue and then gradually rises again. The rotation always remains of a small order as one would expect from considering the small magnetisability of the material.

Two mirrors on the same piece, obtained by grinding at right angles to one another, gave results in good agreement as is shown by tables 1 and 2.

<sup>1)</sup> P. WEISS, Journ. de Physique (4), 9, p. 373, 1910.

<sup>2)</sup> H. DU BOIS, Wied. Ann. 39, p. 25, 1890. Phil. Mag. (5) 29 p. 253, 1890.

<sup>3)</sup> E. WEDEKIND, Zeitschr. für Physik. Chemie 66, p. 614, 1909.

T A B L E 1.

$\varepsilon = f(\lambda)$		$Mn_4Sn$ . (saturated)		TAMMANN
$N$	$\lambda$ ( $\mu\mu$ )	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \partial\varepsilon$
20	435	- 14,8	- 2,24'	0,07' = 3,1 ‰
20	466	- 5,0	- 0,75	0,03 = 4 „
20	503	- 7,9	- 1,18	0,02 = 1,4 „
20	567	- 20,2	- 3,03	0,02 = 0,7 „
20	615	- 28,4	- 4,26	0,02 = 0,5 „
20	675	- 36,8	- 5,52	0,13 = 0,25 „

T A B L E 2.

$\varepsilon = f(\lambda)$		$Mn_4Sn$ (saturated)		TAMMANN
$N$	$\lambda$ ( $\mu\mu$ )	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \partial\varepsilon$
15	466	- 5,0	- 0,75'	0,05' = 6,7 ‰
15	530	- 13,3	- 2,00	0,03 = 1,3 „
12	567	- 20,0	- 3,00	0,04 = 1,3 „
15	615	- 28,4	- 4,26	0,04 = 1 „

*Manganese-antimonide* (Mn 35, Sb 65 = Mn Sb nearly). The material of Prof. TAMMANN showed a strong negative rotation which reached its

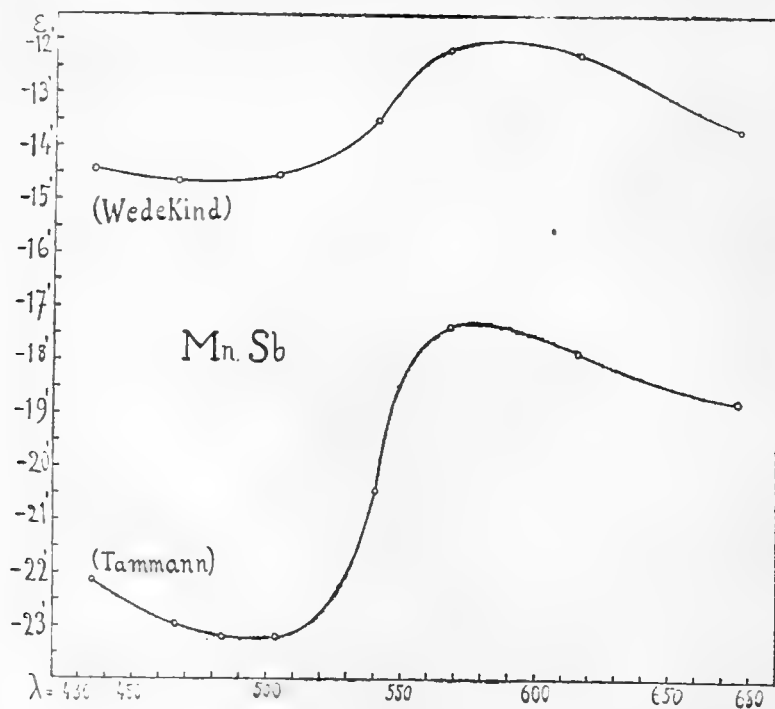


Fig. 2.

numerically highest point in the blue-green and then fell steeply in the green passing through a minimum at about  $580 \mu\mu$ ; it then slowly increased again as it approached the red (Fig. 2).

T A B L E 3.  
 $\varepsilon = f(\lambda)$  *MnSb* (saturated) TAMMANN

$N$	$\lambda (\mu\mu)$	$L$ (mm)	$\varepsilon$ (min.)	$\pm \partial\varepsilon$
40	435	— 148,9	— 22,35'	0,15' = 0,75%
35	466	— 153,5	— 23,02	0,06 = 0,25 „
25	483	— 154,7	— 23,21	0,04 = 0,17 „
25	503	— 154,6	— 23,19	0,03 = 0,13 „
40	530	— 136,4	— 20,46	0,03 = 0,15 „
27	567	— 115,7	— 17,36	0,01 = 0,06 „
25	615	— 119,0	— 17,86	0,02 = 0,11 „
35	675	— 125,0	— 18,75	0,02 = 0,11 „

A second specimen of *MnSb* coming from Prof. WEDEKIND gave a similar dispersion curve agreeing in character with the above. The rotation however always remained smaller than in the case of the first specimen. It can therefore probably be assumed that this corresponds better to the ferromagnetically best compound *MnSb*, whose existence has lately been established with great probability by HILPERT and DIECKMANN<sup>1)</sup>.

T A B L E 4.  
 $\varepsilon = f(\lambda)$  *MnSb* (saturated) WEDEKIND

$N$	$\lambda (\mu\mu)$	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \partial\varepsilon$
30	435	— 96,1	— 14,41'	0,16' = 1,1%
25	466	— 97,1	— 14,57	0,09 = 0,6 „
20	503	— 97,0	— 14,55	0,05 = 0,3 „
21	530	— 91,0	— 13,53	0,03 = 0,2 „
20	567	— 80,9	— 12,14	0,01 = 0,1 „
20	615	— 81,7	— 12,25	0,02 = 0,2 „
21	675	— 87,5	— 13,14	0,05 = 0,4 „

<sup>1)</sup> Cf. KŌTARŌ HONDA loc. cit. E. WEDEKIND, Chem. Ber. 40 p. 1266, 1907  
S. HILPERT and TH. DIECKMANN, Chem. Ber. 44 p. 2833, 1911.

*Manganese-bismuthide*<sup>1)</sup> (MnBi). The rotation, which was negative at both ends of the spectrum (Fig 3), reached a positive maximum at 530  $\mu\mu$ . Points of inversion were found at 468  $\mu\mu$  and 617  $\mu\mu$ . Although the mirror was not very bright I was yet able to measure the rotation fairly accurately in spite of its small amount.

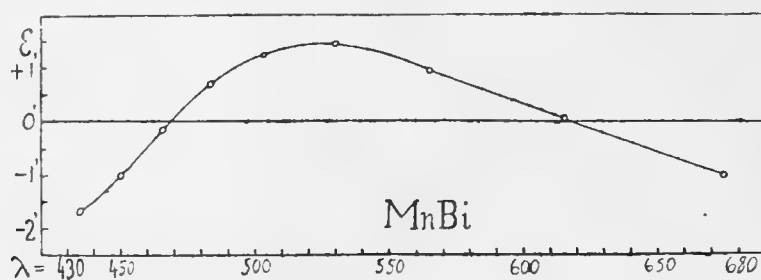


Fig. 3.

T A B L E 5.

$\varepsilon = f(\lambda)$	<i>Mn Bi</i> (saturated)			HILPERT
<i>N</i>	$\lambda$ ( $\mu\mu$ )	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \delta\varepsilon$
25	435	- 11,0	- 1,65'	0,13' = 7,7 ‰
25	450	- 6,7	- 1,00	0,07 = 7,3 ‰
50	466	- 1,1	- 0,16	0,04 = 22,0 ‰
25	483	+ 4,8	+ 0,72	0,05 = 6,5 ‰
21	503	+ 8,4	+ 1,26	0,03 = 2 ‰
21	530	+ 9,9	+ 1,48	0,03 = 2 ‰
21	567	+ 6,3	+ 0,94	0,03 = 2,8 ‰
70	615	+ 0,3	+ 0,045	0,015 = 33,3 ‰
30	675	- 6,6	- 0,99	0,02 = 2 ‰

## IRON COMPOUNDS.

*Iron carbide* ( $\text{Fe}_3\text{C}$ , Cementite). As the material contained for the most part cementite in needle-like crystalline layers mixed with other substances, the mirror was treated with sulphurous acid so that the cementite surfaces did not change their reflecting power while the other constituents were strongly darkened. Measurements carried out on six different parts of the surface yielded somewhat different results. All the curves however show a certain similarity viz. a very

<sup>1)</sup> S. HILPERT and TH. DIECKMANN, Chem. Ber. **44** p. 2831, 1911. E. WEDEKIND and A. VEIT, Chem. Ber. **44** p. 2665, 1911.

strong negative rotation having a numerical maximum in the violet and indicating a decrease towards the ultra-violet. It falls steeply in the blue region until the green or yellow-green is reached and then increases again towards the red. The carbon atom of the carbide accordingly produces a considerable change in the dispersion curve, compared with that of pure iron (table 12). Four of the curves are represented in fig. 4 and tab. 6 to 9. The two other places gave a smaller rotation. A consideration of the etched figures on the surface show that a better agreement for such a complicated structure can hardly be expected. On this account the investigation of alloys appears altogether more difficult than in the case of well defined compounds.

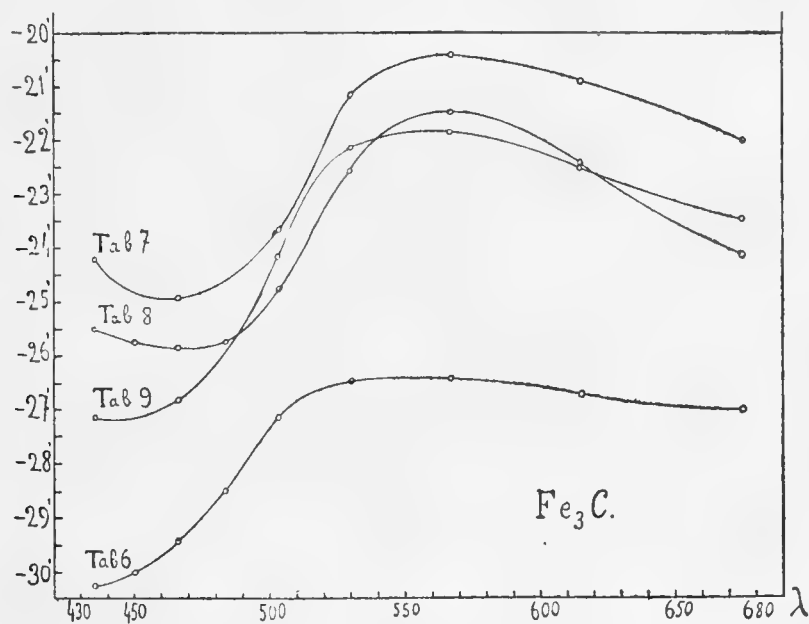


Fig. 4.

TABLE 6.

$\varepsilon = f(\lambda)$		Iron carbide (saturated)		HILPERT
$N$	$\lambda (\mu\mu)$	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \sigma\varepsilon$
30	435	— 201,9	— 30,28'	0,05' = 0,17%
25	450	— 200,0	— 30,00	0,03 = 0,10 „
20	466	— 196,3	— 29,42	0,02 = 0,07 „
20	483	— 189,8	— 28,48	0,02 = 0,07 „
20	503	— 180,8	— 27,13	0,02 = 0,07 „
20	530	— 176,3	— 26,45	0,01 = 0,04 „
20	567	— 176,0	— 26,40	0,02 = 0,08 „
20	615	— 177,7	— 26,66	0,01 = 0,04 „
20	675	— 180,1	— 27,01	0,03 = 0,11 „

T A B L E 7.

$N$	$\lambda (\mu\mu)$	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \partial\varepsilon$
25	435	-161,4	-24,20	0,10' = 0,40%
25	466	-166,1	-24,91	0,05 = 0,2 „
20	503	-157,8	-23,66	0,07 = 0,3 „
20	530	-141,1	-21,17	0,05 = 0,2 „
20	567	-136,0	-20,40	0,02 = 0,1 „
20	615	-139,6	-20,91	0,02 = 0,1 „
20	675	-146,8	-22,02	0,04 = 0,2 „

T A B L E 8.

$N$	$\lambda (\mu\mu)$	$\hat{L}$ (mm)	$\varepsilon$ (min.)	$\pm \partial\varepsilon$
25	435	-170,0	-25,50'	0,05' = 0,20%
25	450	-171,7	-25,75	0,03 = 0,1 „
20	466	-172,1	-25,81	0,03 = 0,1 „
20	483	-171,7	-25,75	0,03 = 0,1 „
20	503	-165,0	-24,76	0,03 = 0,1 „
20	530	-150,3	-22,55	0,02 = 0,1 „
20	567	-143,1	-21,46	0,02 = 0,1 „
20	615	-149,4	-22,40	0,03 = 0,1 „
20	675	-161,0	-24,14	0,03 = 0,1 „

T A B L E 9.

$N$	$\lambda (\mu\mu)$	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \partial\varepsilon$
30	435	-181,0	-27,15'	0,07' = 0,3%
25	466	-178,7	-26,79	0,03 = 0,2 „
30	503	-161,0	-24,14	0,04 = 0,1 „
25	530	-147,5	-22,13	0,01 = 0,04 „
25	567	-145,4	-21,81	0,01 = 0,05 „
20	615	-150,0	-22,50	0,01 = 0,04 „
20	675	-156,3	-23,44	0,03 = 0,1 „

*Normal Pyrrhotine* ( $\text{Fe}_7\text{S}_8 = (\text{FeS})_5 \text{Fe}_2\text{S}_3$ , from Morro Velho, Brazil). The piece with which I made my measurements was polished, in the first case, parallel to the magnetic plane and in the second case in a plane normal to this and to the direction of easiest magnetisation <sup>1)</sup>. The first mirror, as was to be expected, showed no rotation whatsoever. On the second surface however a positive rotation of the order of one minute was to be observed for the whole region of the spectrum. Even at the ends of the spectrum no indication of an inflection in the dispersion curve could be found: (perhaps a trace of an increase in the violet). I repeated the same measurements thereupon more accurately, the slit of the monochromator being widened, using a brighter yellow and blue illumination. The field here amounted to at least 12 kgs.

T A B L E 10.

$\varepsilon = f(\lambda)$		<i>Normal Pyrrhotine</i> (saturated)		WEISS
<i>N</i>	$\lambda$ ( $\mu$ )	$L$ (mm)	(min.)	$\pm \partial z$
35	435	+ 6,6	+ 0,98'	0,04' = 4 1/2
30	»	+ 6,7	+ 1,00	0,05 = 5 »
25	466	+ 6,3	+ 0,94	0,04 = 4 »
20	483	+ 6,6	+ 0,97	0,04 = 4 »
20	503	+ 6,4	+ 0,95	0,03 = 3 »
20	530	+ 6,5	+ 0,96	0,03 = 3 »
20	567	+ 6,4	+ 0,95	0,02 = 2 »
20	615	+ 6,6	+ 0,97	0,03 = 3 »
25	675	+ 6,3	+ 0,94	0,04 = 4 »
30	»	+ 6,6	+ 0,97	0,03 = 3 »
20	blau	+ 6,4	+ 0,94	0,02 = 2 »
20	»	+ 6,6	+ 0,96	0,01 = 1 »
20	gelb	+ 6,4	+ 0,95	0,02 = 2 »
20	»	+ 6,5	+ 0,96	0,01 = 1 »

*Compact magnetic pyrite* (presumably from Obermais, Tyrol). A naturally reflecting surface was previously found by du Bois to show

<sup>1)</sup> According to the above formula this substance ought to be regarded as Sulphopentaferroferrite. P. WEISS, Journ. de Phys. (4) 4 p. 469, 1905 finds for the saturation value of magnetisation about 60 to 75 C.G.S.

no effect; this was irregular and moreover parallel to the magnetic plane. In the present work, as in the case of pyrrhotine, a mirror was obtained by grinding, normal to the above. It gave a small positive rotation of some tenths of a minute.

*Amorphous iron sulphide* (Fe S). This substance, which is not ferromagnetic, was also investigated by du Bois l. c. in 1889. The same mirror now also gave a negative result. Should a rotation exist, it must be smaller than 0,3'.

*Cerium-iron*. The dispersion in the case of pyrophorous cerium-iron of unknown composition exhibited nothing exceptional. The rotation increased a little on passing from violet to red. The material was not quite saturated.

T A B L E 11.

$\varepsilon = f(\lambda)$ <i>Cerium-iron</i> (nearly saturated)				
$N$	$\lambda$ ( $\mu\mu$ )	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \partial\varepsilon$
25	435	— 33,9	— 5,09'	0,05' = 1 ‰
20	466	— 36,7	— 5,50	0,04 = 0,7 „
20	503	— 39,8	— 5,97	0,02 = 0,3 „
20	530	— 41,5	— 6,22	0,01 = 0,2 „
20	567	— 42,7	— 6,41	0,01 = 0,2 „
20	615	— 43,5	— 6,52	0,02 = 0,3 „
25	675	— 44,0	— 6,60	0,03 = 0,4 „

T A B L E 12.

$\varepsilon = f(\lambda)$ <i>Iron</i> (unsaturated)				WEISS
$N$	$\lambda$ ( $\mu\mu$ )	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \partial\varepsilon$
25	435	— 126,4	— 18,96'	0,10' = 0,5 ‰
20	483	— 131,0	— 19,65	0,05 = 0,25 „
20	530	— 136,6	— 20,47	0,03 = 0,15 „
20	567	— 141,7	— 21,25	0,02 = 0,09 „
20	615	— 149,5	— 22,42	0,02 = 0,09 „
20	675	— 164,6	— 24,70	0,03 = 0,12 „



## METALS.

*Iron* (electrolytic). The dispersion curve remains throughout in the negative region, numerically increasing from violet to red with an indication of a minimum in the ultraviolet. The iron investigated by du Bois, loc. cit., showed a dispersion of a similar but more marked character. The material was not saturated.

*Cobalt*. The curve showed a flat numerical minimum in the blue-green near 530  $\mu\mu$ . Otherwise there is nothing particular to be noticed. In the case of the impure cobalt investigated by du Bois the minimum was even less marked.

T A B L E 13.

$\varepsilon = f(\lambda)$		<i>Cobalt</i> (unsaturated)		WEISS
$N$	$\lambda(\mu\mu)$	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \delta\varepsilon$
25	435	— 141,7	— 21,25'	0,12' = 0,56 <sup>0</sup> / <sub>0</sub>
20	483	— 134,6	— 20,20	0,05 = 0,25 „
20	530	— 131,5	— 19,74	0,02 = 0,10 „
20	567	— 132,8	— 19,92	0,01 = 0,05 „
20	615	— 135,3	— 20,28	0,01 = 0,05 „
20	675	— 141,0	— 21,15	0,03 = 0,14 „

*Nickel*. The curve showed a minimum in the yellow but otherwise no singularities. The dispersion of the original nickel-mirror of du Bois was exactly proportional to this. The metal was not completely saturated.

T A B L E 14.

$\varepsilon = f(\lambda)$		<i>Nickel</i> (nearly saturated)		WEISS
$N$	$\lambda(\mu\mu)$	$L$ (mm)	$\varepsilon$ (min.)	$\pm \delta\varepsilon$
20	435	— 57,6	— 8,64'	0,05' = 0,56 <sup>0</sup> / <sub>0</sub>
20	483	— 56,0	— 8,39	0,02 = 0,24 „
20	530	— 54,3	— 8,15	0,01 = 0,12 „
20	567	— 53,3	— 8,00	0,01 = 0,12 „
20	615	— 55,5	— 8,32	0,01 = 0,11 „
20	675	— 59,7	— 8,96	0,02 = 0,22 „

**Physics.** — “*The effect of temperature and transverse magnetisation on the resistance of graphite.*” By DAVID E. ROBERTS. (Communicated by Prof. H. E. J. G. DU BOIS).

The investigations of GRUNMACH and WEIDERT<sup>1)</sup>, PATTERSON<sup>2)</sup> and others on the effect of transverse magnetisation on electrical resistance show that paramagnetic and diamagnetic metals exhibit an increase of resistance when magnetised, while the three ferromagnetic metals, at least in sufficiently strong transverse fields, show a decrease. Although as yet no simple relation may be given between the order of magnitude of this effect and the corresponding magnetic susceptibility, it may be noticed that the effect increases in the ratio of one to a hundred as we pass from paramagnetic tantalium to diamagnetic cadmium and suddenly again a thousandfold as we pass on to bismuth. This element, as is well known, possesses rather a high diamagnetic specific susceptibility ( $-1,40 \cdot 10^{-6}$ ). Soon after MORRIS OWEN<sup>3)</sup> found Ceylon graphite to show the highest value yet observed, Dr. W. J. DE HAAS was led, by analogy, to anticipate that graphite might exhibit a variation of resistance of an even higher order when magnetised and suggested to me to search for the effect. The preliminary experiments<sup>4)</sup> performed with powdered graphite pressed into a thin plate, with irregularly shaped pieces and with ordinary pencils amply satisfied expectation and justified an extended investigation of the phenomenon.

Well defined crystals of graphite are exceedingly rare and could not be procured; the ordinary material occurs in lamellar agglomerations, cleavable with great ease along surfaces parallel to the base of the hexagonal system. From a chemical point of view the structure is possibly very complicated; graphite is generally considered, above  $372^\circ$ , the most stable of the three allotropic carbon modifications.

The conductivity for heat of this substance has lately been studied by KOENIGSBERGER and WEISS<sup>5)</sup>. The resistivity as formerly determined by several observers<sup>6)</sup> is as follows:

<sup>1)</sup> L. GRUNMACH and F. WEIDERT, *Ann. der Phys.* **22** p. 141, 1907.

<sup>2)</sup> J. PATTERSON, *Phil. Mag.* (6) **3** p. 643, 1902.

<sup>3)</sup> MORRIS OWEN, *Versl. Afd. Natuurk.* **20** p. 673, 1911. *Ann. der Physik.* **37** p. 657, 1912.

<sup>4)</sup> When magnetised transversely in a field of 20 kilogauss, the compressed powdered Ceylon graphite gave an increase in resistance of 52%; an irregularly shaped piece gave 219%; HB and 5B pencils by A. W. FABER gave only 3% increase.

<sup>5)</sup> J. KOENIGSBERGER and J. WEISS, *Ann. der Physik.* **35** p. 27, 1911. *Verh. d. Deutsch. physik. Ges.* **14** p. 9, 1912.

<sup>6)</sup> See *Handb. der Anorg. Chemie* **3** (2 Abtl.) p. 54, 1909.

Graphite from Ceylon	at 0°	12.10 <sup>-4</sup>	ohm per cm <sup>3</sup>
„ „ Siberia	„ „	11.10 <sup>-4</sup>	„ „ „
„ „ Greenland	„ 15°	4.10 <sup>-4</sup>	„ „ „

The best of my samples gave a resistivity as small as  $0,5 \cdot 10^{-4}$ , i.e. roughly about half that of mercury ( $0,96 \cdot 10^{-4}$  at  $18^\circ$ ): this *increased* with rise of temperature by about 0,001 per degree. The resistivity of amorphous carbon has always been found to be much larger and is well-known to *decrease* with rise of temperature; the coefficient diminishes, however, as the transformation into the graphitic modification proceeds<sup>1)</sup>, although it has never been observed to change its sign.

With regard to the effect of magnetisation PATTERSON l. c. found the resistance of a glow-lamp filament to increase by 0,027 percent in a transverse field of 25 kilogauss. According to CLAY<sup>2)</sup> the resistivity of such a filament decreases by 24 % on heating from  $-255^\circ$  to  $0^\circ$ . LAWS<sup>3)</sup> has investigated the effect for transverse magnetisation of glow-lamp filaments, pencils and graphite without finding it to be of a high order. He found, at ordinary temperatures, the increase of resistance of the graphite in a field of 11 kilogauss to be about 1 % of the resistance when outside the field, while at the temperature of liquid air the effect was increased threefold. Within this small range the increase of resistance was found proportional to the square of the field and between the temperatures  $18^\circ$  and  $-186^\circ$  inversely proportional to the absolute temperature. As will be seen these results are not in agreement with those found in the present research.

#### EXPERIMENTAL ARRANGEMENT.

The specimens most used in this investigation were prepared from the same Ceylon graphite as that used by OWEN in his researches on its thermo-magnetic properties; a chemical analysis has not yet been made. Short rectangular pieces (7—10 mm. long, 1—2 mm. wide and 0,1—0,5 mm. thick) were obtained by careful cleavage and those selected for investigation which appeared of most pronounced and uniform crystalline structure. For the determination of the effect of transverse magnetisation they were, in general, supported in the magnetic field so that the cleavage planes were perpendicular to the field i. e. the crystalline axis was parallel to the lines of force. On supporting the pieces freely in a magnetic field it was observed

<sup>1)</sup> See Handb der Physik 4 p. 380, 1905. G. WIEDEMANN, Elektrizität, 1 p. 539, 1882.

<sup>2)</sup> J. CLAY. Dissert., Leiden 1908.

<sup>3)</sup> S. C. LAWS. Phil. Mag. (6) 19, p. 694, 1910; his graphite was obtained from the MORGAN Crucible Co., London.

that they moved so that the crystalline axis set itself perpendicular to the field, this axis thus coinciding with the direction of maximum diamagnetic specific susceptibility, which according to OWEN may reach — 15 millionths.

The magnetic field of the latest large type model of the DU BOIS half-ring electromagnet was used. To obtain the higher fields at ordinary temperatures special prism-shaped pole end-pieces were used — 13 mm. long and 1,2 mm. wide. — With these end-pieces (0,7 mm. apart) and a pair of extra polar coils a field of 50 kilogauss could be easily attained. For observations at low and high temperatures the same arrangement was used as that adopted by DU BOIS and WILLS in conjunction with the large type electromagnet<sup>1)</sup>. The magnetic fields were measured by means of an exploring coil and a ballistic galvanometer<sup>2)</sup> in the usual way. It was assumed provisionally that the fields were appreciably the same at all the temperatures used for a given current through the electromagnet.

The resistance of the graphite specimens, both in and out of the field, was determined by a potentiometer method<sup>3)</sup>, being compared directly with known resistances (0,1—1,0 ohm). The current through the graphite during a series of measurements was varied between 2 and 0,5 milliamperes according to its resistance. In order to eliminate thermo-electric junction effects the current in the main circuit as well as the potentiometer connections were successively reversed. The changes of resistance involved being considerable it was found necessary to adjust the sensitiveness of the potentiometer arrangement during a single series of readings; this was initially sufficient to detect differences of  $\frac{1}{10000}$  ohm. Small irregular variations in the resistance of a particular specimen were observed after it was subjected to the action of magnetic fields or to widely different temperatures. This change, however, amounted in general to less than 1%. Through the kindness of Dr. HOFFMANN the resistance of specimen G. 15 — that used in the experiments at different temperatures — was re-determined at 18° in the Phys. Techn. Reichsanstalt by means of DIESELHORST'S "compensation apparatus"<sup>4)</sup> and a differential galvanometer; good agreement was found. Some of the preliminary measurements had been made with WHEATSTONE'S bridge method and, when repeated potentiometrically, practically the same results were obtained.

<sup>1)</sup> H. DU BOIS. Ztschr. für Instr.kunde **31**, p. 362, 1911.

<sup>2)</sup> H. DU BOIS. The magnetic circuit in theory and practice, p. 300, London 1896.

<sup>3)</sup> F. KOHLRAUSCH, Prakt. Physik. 11 Auflage p. 422, 1910.

<sup>4)</sup> H. DIESELHORST, Zeitschr. für Instr.kunde. **26** pp. 173, 297, 1906; **28** pp. 1, 38, 1908.

## EXPERIMENTS AT ORDINARY TEMPERATURE [18°].

About twenty specimens of Ceylon graphite were investigated, which all gave variations of resistance of a high order, the increase of resistance in a field of 20 kilogauss varying however between 300 and 500% of the resistance in zero field. Considering the difficulty of obtaining specimens of graphite of definite crystalline structure and having regard to the impurities occurring in the natural substance these variations in the magnitude of the effect are not surprising. About five specimens, which gave a variation of resistance of greatest order were investigated more particularly; by analogy with the well-known behaviour of more or less pure bismuth <sup>1)</sup> the assumption appeared justifiable that these were more likely to be pure and perhaps of more uniform crystalline structure. Some of the specimens were supported free between thin mica or glass plates; when imbedded in sodium silicate, collodion or Canada balsam allowed afterwards to solidify they did not experience any change in the magnitude of their increase of resistance in the magnetic field, thus eliminating any doubts that the effects were due to bodily strains in the graphite. In the final experiments at different temperatures the graphite pieces were supported by fine flexible wires between thin mica plates so as to avoid any strain due to possible expansion or contraction. The specimens could be mounted with their connections so that the total thickness amounted to less than 0.7 mm, thus enabling them to be examined in fields up to 50 kilogauss. Some of

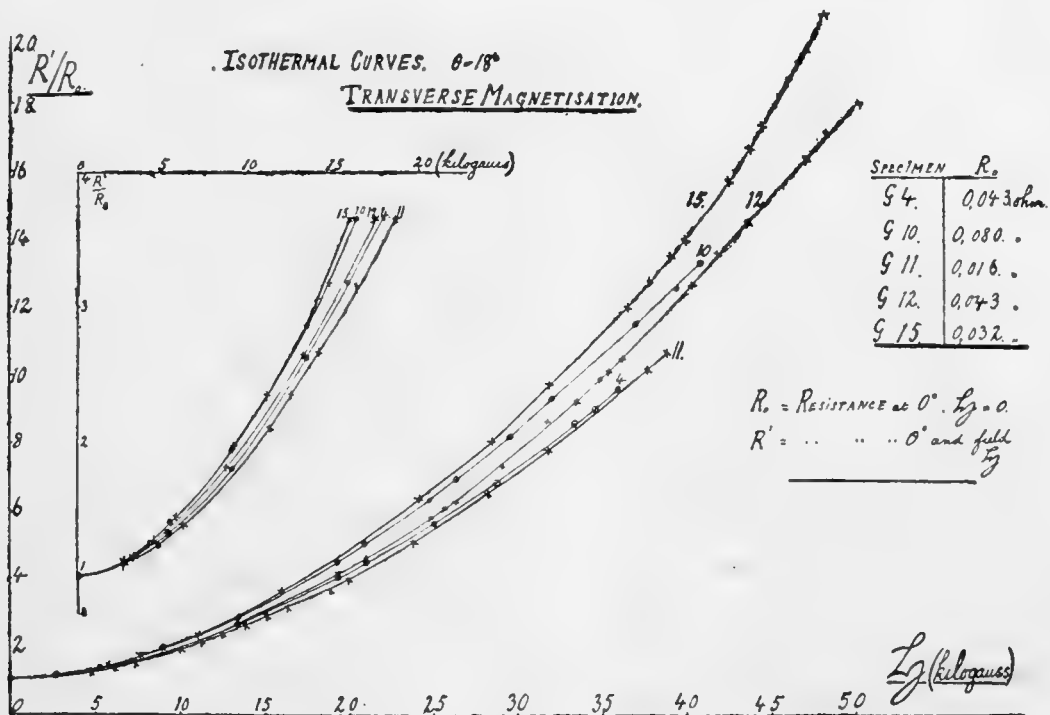


Fig. 1.

<sup>1)</sup> F. C. BLAKE, Ann. der Physik 28 p. 449 1909.

the isothermal curves obtained for different specimens, at 18°, with the cleavage plane normal to the field, are shown in Fig. 1.

Attempts to identify the curves with such equations as

$$\frac{R'}{R_0} = \frac{R}{R_0} + b\mathfrak{H} + c\mathfrak{H}^2 + \dots$$

failed; it was found however that all the curves obtained at ordinary temperatures could, well within experimental errors, be represented by the formula

$$\frac{R'}{R_0} = \frac{R}{R_0} + A\mathfrak{H}^n \quad \dots \quad (1)$$

where  $R_0$ , resistance at 0° for  $\mathfrak{H} = 0$ ,

$R$ , „ „  $\theta^\circ$  for  $\mathfrak{H} = 0$ ,

$R'$ , „ „  $\theta^\circ$  in transverse field  $\mathfrak{H}$ .

$A, n$  Constants.

Owing to the difficulty of determining the dimensions of the specimens it is unfortunately impossible to give their absolute resistivity with any exactitude.

From equation (1) we have, taking logarithms

$$\log \frac{R' - R}{R_0} = \log A + n \log \mathfrak{H}$$

which can be represented by a straight line, the coordinates being  $\log (R' - R) R_0$  and  $\log \mathfrak{H}$ .

The values of  $\log (R' - R) R_0$  and  $\log \mathfrak{H}$ , corresponding to the curves shown in fig. 1, when plotted were found to lie on straight lines practically parallel to one another, indicating that  $n$  is the same constant for each of these specimens. In the case of specimen G. 15 — the one which gave an increase of the greatest order — equation (1) did not hold as well as for the other specimens although the mean value of  $n$  was the same for this as for the others.

T A B L E 1.

Isothermals at 18°		
Specimen	$R_0$	$R'/R_0 = R/R_0 + A\mathfrak{H}^n$
G. 4	0.0430 ohm.	1.01 + 0.0171 $\mathfrak{H}^{1.745}$
G. 10	0.0792 „	1.01 + 0.0205 $\mathfrak{H}^{1.745}$
G. 11	0.0162 „	1.004 + 0.0162 $\mathfrak{H}^{1.745}$
G. 12	0.0430 „	1.014 + 0.0188 $\mathfrak{H}^{1.745}$
G. 15	0.0316 „	1.02 + 0.0214 $\mathfrak{H}^{1.745}$

The values of  $A$  and  $n$  obtained for the different specimens are given in Table 1. For each specimen  $n = 1.74^5$  1).

A specimen was also prepared for investigation from another piece of Ceylon graphite out of the laboratory collection. This graphite very easily split up along its cleavage surfaces but pieces of uniform structure of suitable form were difficult to obtain. The best piece I could prepare gave an increase of resistance of only 182% in a field of 20 kilogauss, the resistance out of the field being 0.0427 Ohm.

A piece of graphite from Himbuluwa (Ceylon), which was investigated, on the other hand, gave quite different results. The upper side of this graphite possessed a quite smooth and polished surface underneath which however it appeared to be of a fine granular structure. A thin piece of this upper layer was removed and the variation of its resistance found when transversely magnetised. An increase of resistance of 220% was observed in a field of 20 Kgs, the resistance out of the field being 0.0786 ohm. A thin piece removed from the under side of the same material, and having a high natural polish on *both* of its cleavage surfaces gave the anomalous results. Its resistance outside the field was several hundred ohms and diminished very rapidly with increase of temperature. In a magnetic field however no change in its resistance could be observed, while rough experiments indicated that it was apparently paramagnetic; no test for the presence of ferroginous impurities was made.

Specimen G 12 was also tested with its cleavage plane parallel to a transverse field, the crystallic axis being therefore at right angles to the lines of force. In a field of 26 kgs the value  $R'/R_0$  was found to be only 1.15 while for the usual position this ratio is rather more than 6. This evidently proves the necessity for very accurate adjustment of the angle between the crystallic and field axes<sup>2)</sup>; an analogous question is known to arise in the behaviour of nickel and other ferromagnetic wires.

#### EXPERIMENTS AT LOW AND HIGH TEMPERATURES.

Observations were taken at temperatures of  $-179^\circ$ ,  $0^\circ$ ,  $+18^\circ$ ,  $+95^\circ$  and  $+179^\circ$ , the field being varied from 0 to 40 kilogauss.

1) Within the experimental errors the exponent may also be  $n = \sqrt[5]{3} = 1.732$  or  $n = 7/4$ .

2) The effect of longitudinal magnetisation was also observed. The increase of resistance involved was found to be independent of the direction of the current and of the same order as that observed in this last described position. Experiments are in progress to study the effect in both these cases at different temperatures.

The method of measurement was the same as at  $18^\circ$ ; the determinations afforded no difficulty, the resistances being quite steady. At the lower and higher temperatures thermo-electric effects were sometimes evident but by successive reversals these were eliminated. It was incidentally observed that these thermo-electric effects — when occurring at the connections of the graphite and therefore within the magnetic field — were also influenced by the field <sup>1)</sup>. Thus in one case the thermo-electric effect was increased fourfold by a field of 38 kgs. For all the specimens examined (with the exception of the piece from Himbuluwa) the resistance of the graphite out of the field was found to *increase* with the temperature, the coefficient of increase of resistance being of the order 0,001 per degree. The ordinary temperature curve  $R = \text{funkt. } (\theta)$  for  $H = 0$  is given in Fig. 2 for G 15. Very

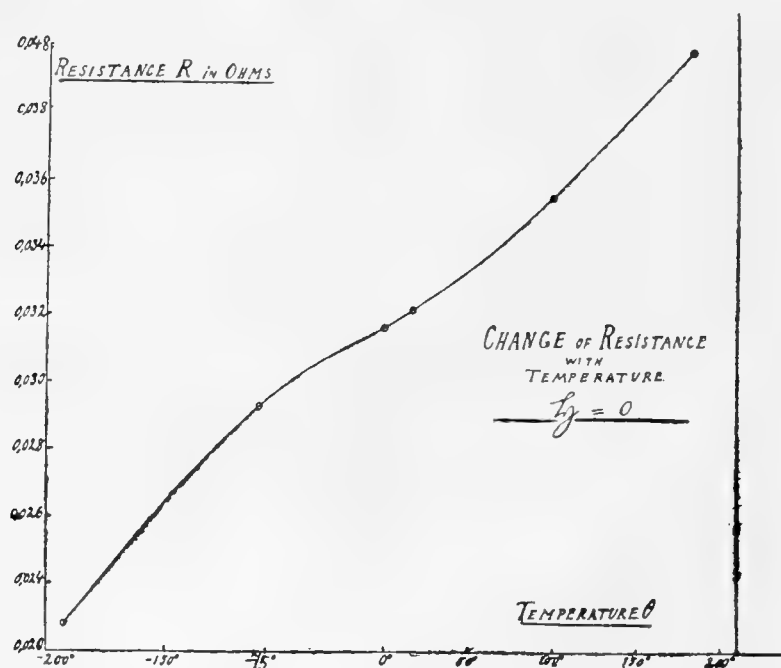


Fig. 2.

nearly the same type of curve was obtained in the case of specimen G 11. It is interesting to compare this with the curves obtained by KAMERLINGH ONNES and NERNST <sup>2)</sup>. The temperature during a series of readings, the graphite being in the field, was determined as follows. Before commencing, the current required to be sent in the reverse direction through the magnet to reduce the residual field to zero, was determined. Then, to measure the temperature, the graphite

<sup>1)</sup> These effects are being subjected to further detailed investigation.

<sup>2)</sup> H. KAMERLINGH ONNES, Versl. Afd. Nat. 19. p. 1187, 1911. W. NERNST, Sitz. Ber. Berl. Akad. p. 306, 1911.



being in position, this reverse current was set up and the resistance of the graphite found. The temperature of the graphite was then deduced from the temperature curve ( $\mathfrak{H} = 0$ ) fig. 2. Owing to the difficulty of exactly getting rid of the residual field without setting up a field in the opposite direction, and on account of the small change of resistance with temperature, this method of determining the temperature does not seem to be susceptible of great accuracy. The isothermals at low and high temperatures were determined for G 11 and G 15. Except for the difference in the magnitude of the changes of resistance concerned similar results were found. The results obtained with specimen G 15 are shown as isothermal curves (fig. 3) from which the so-called isopedic curves ( $\mathfrak{H} = \text{constant}$ ) may

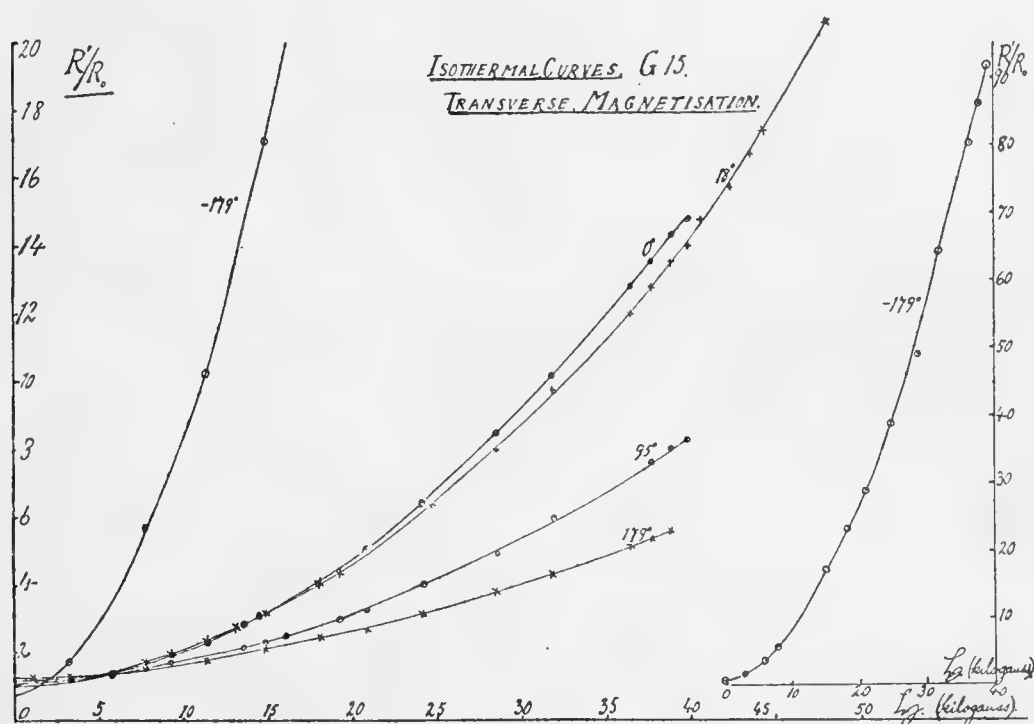


Fig. 3.

easily be deduced. As will be seen, the increase of resistance is much greater at low temperatures. At the temperature of liquid air the increase is 9300 % for a field of 38,8 kgs, the increase at 18° being 1250 %.

The isothermal curves for the lower temperatures cannot be represented by an equation of the form (1); at higher temperatures this seems to be the case, although more accurate measurements appear desirable.

**Physics.** — “*Translation series in line-spectra.*” By T. VAN LOHUIZEN.  
(Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of May 25, 1912).

In my preceding communication<sup>1)</sup> I told already how I had succeeded in discovering series in the spectra of Tin and Antimony by making use of a model which was the result of a spectral formula found by me empirically, which formula was based on the fundamental thought: “Every series in a line-spectrum of whatever element can be represented by one and the same curve when the frequencies are considered as function of the parameter, and the curve refers every time to another system of axes.”

I will now show how this fundamental thought may be serviceable to arrange the series of systems of the different elements in better order. It is true that some order has already been brought in the great material of observation<sup>2)</sup> by the discovery of numerous series by RYDBERG, KAYSER and RUNGE and others, and recently particularly by the “Kombinationsprinzip”, discovered by RITZ, but it is exactly this great number of series and combinations that threatens to destroy the order and bring confusion. If we consult, e. g. a treatise by DUNZ<sup>3)</sup> which was recently published, we find there a great quantity of material of observation arranged according to RITZ’s spectral formula and the “Kombinationsprinzip”, but it appears already very soon that specially for the numerous combinations the order leaves a good deal to be desired. It is impossible to have a survey of the matter. That this way of arrangement is not the only one, is shown by MOGENDORFF<sup>4)</sup> in his communication on “Summational and differential vibrations in line-spectra”, in which most of the combinations are indicated as summational and differential vibrations. Though the system is by no means lucid here either, yet we will for a moment retain the idea of differential vibrations. Already before PASCHEN<sup>5)</sup> had about the same idea when he says: “Die Linien eines Seriensystems sind darstellbar durch eine Anzahl von Termen, deren Differenzen die Wellenzahlen (bzw. Schwingungszahlen) existierender Linien geben.”

The first thought of this sentence is already found in RYDBERG, where he takes the asymptote of the principal series as a special

<sup>1)</sup> These Proc. p. 31.

<sup>2)</sup> Cf. KAYSER, Handbuch der Spectroscopie Bd. V and EXNER and HASCHKE, Die Spektren der Elemente bei normalem Druck.

<sup>3)</sup> Unsere Kenntnisse von den Seriengesetzen der Linienspektren.

<sup>4)</sup> Proc. Royal Acad. Amst. Nov. 25, 1911.

<sup>5)</sup> Jahrbuch der Radioaktivität und Elektronik Bd. 8, Heft 1.

value of the fraction which occurs in the formula of the 2<sup>nd</sup> subordinate series. LORENTZ<sup>1)</sup> too holds the same idea in his theory on the ZEEMAN-effect, where he says: "In connection with this, it should also be noticed that, in RYDBERG's formulae, every frequency is presented as the difference between two fundamental ones". A more independent meaning is assigned to these fractions by HICKS<sup>2)</sup>, who gives them the name of "sequences".

He distinguishes viz. four kinds of them:

1. Principal (*P*) sequence.
2. Sharp (*S*) sequence.
3. Diffuse (*D*) sequence.
4. Fundamental (*F*) sequence.

In agreement with the theory given by RITZ<sup>3)</sup> HICKS expresses himself as follows<sup>4)</sup>:

"It appears, that, whatever the kinetic configuration may be, which is the source of the vibrations, the light periods depend on the difference of frequency of *two* systems each with distinguishing train of frequencies".

In DUNZ<sup>5)</sup> we find the values of these systems calculated and indicated as  $mp$ ,  $ms$ ,  $md$ , and  $m\Delta p$ , in which we recognize HICKS's sequences, and about which we may notice that when we confine ourselves to one component, *all the series and combinations are formed from these four "sequences"*.

In the following manner this system may at once be reduced to order, so that it is easy to survey:

All the series and combinations may be graphically represented by one and the same curve, which is subjected to four different rotations with regard to the original system of axes. All the series that are represented by curves of equal rotation, belong together and differ only in asymptote. They may be changed into each other by a translation of the curve parallel to the  $y$ -axis. We shall therefore call them *Translation series*. The asymptotes may be found from a curve with the same or with another rotation. So every spectral line is determined by its number on the curve and by the asymptote of this curve.

Before entering into a fuller explanation by means of the annexed plate, I should first point out the necessity of the introduction of

1) Theory of Electrons etc. p. 128.

2) Phil. Trans. 210 A 1911 p. 57 et seq.

3) Magnetische Atomfelder und Serienspektren Ann. d. Phys. 25. 1908 p. 660 et seq.

4) l. c. p. 96.

5) l. c.

an all-including notation. This necessity already appears on a cursory examination of the notations used by PASCHEN (RITZ's notation), HICKS (a modified RYDBERG notation), and MOGENDORFF (in the cited communication), while, as we saw above all three entertain about the same idea about the differential action. Let us now try to bring unity in this by considering the thought they have all in common, viz. that in accordance with RITZ's theory<sup>1)</sup> on the magnetic atomic fields, *every spectral line is brought about by the difference of two actions.*

So in the notation of every spectral line it should be expressed, with what member of what two series (sequences) it is related. For the designation of these series the nomenclature introduced by HICKS<sup>2)</sup> is the most convenient, because the notations *mp*, *ms* etc. exist already also with RITZ's formula.

So we distinguish:

1. Principal series or  $Px$  ( $x = 1 . 2 . 3 . . .$ )
2. Sharp series or  $Sx$  ( $x = 1 . 2 . 3 . . .$ )
3. Diffuse series or  $Dx$  ( $x = 1 . 2 . 3 . . .$ )
4. Fundamental series or  $Fx$  ( $x = 1 . 2 . 3 . . .$ )

The form of these series is somewhat different for the different spectral formulae, but yet there is close agreement. The numerators are the same for all three, (RITZ, MOGENDORFF-HICKS, and mine), viz. the universal constant 109675,0. The roots from the denominators are threeterms. The first term of it is the parameter ( $m$  or  $x$ ), the second a constant ( $a$ ,  $p$ ,  $s$ ,  $d$  or  $\mu$ ), the coefficient of the third term being denoted by ( $b$ ,  $\pi$ ,  $\sigma$ ,  $\delta$  or  $\gamma$ ). Let us now also bring agreement in this, and in imitation of RITZ introduce different, but corresponding symbols for the different series, so for the constant terms resp.  $p$ ,  $s$ ,  $d$ , and  $f$ , and for the last coefficients resp.  $\pi$ ,  $\sigma$ ,  $\delta$ , and  $\varphi$ .

Then the meaning of  $Px$ ,  $Sx$  etc. will be according to the formulae of RITZ, ( $R$ ), of MOGENDORFF-HICKS ( $MH$ ), and according to my formula ( $L$ ): (see table p. 159).

$X$  may be put here: 1 . 2 . 3 . . . The notation, as RITZ introduced it for the 2<sup>nd</sup> subordinate series (1,5; 2,5; 3,5; . . .) should be discarded. It makes the matter difficult to survey. Though for some metals we do get the impression that we have to do with  $x + 0,5 +$  a certain fraction, this is by no means the case for all, and I entirely concur with the conclusion of HICKS<sup>1)</sup>, who has inquired into this matter more closely:

<sup>1)</sup> l. c.

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

	$R$	$MH$	$L$
$Px =$	$\frac{109675.0}{\left(x + p + \frac{\pi}{x^2}\right)^2}$	$\frac{109675.0}{\left(x + p + \frac{\pi}{x}\right)^2}$	$\frac{109675.0}{(x + p + \pi y)^2}$
$Sx =$	$\frac{109675.0}{\left(x + s + \frac{\sigma}{x^2}\right)^2}$	$\frac{109675.0}{\left(x + s + \frac{\sigma}{x}\right)^2}$	$\frac{109675.0}{(x + s + \sigma y)^2}$
$Dx =$	$\frac{109675.0}{\left(x + d + \frac{\delta}{x^2}\right)^2}$	$\frac{109675.0}{\left(x + d + \frac{\delta}{x}\right)^2}$	$\frac{109675.0}{(x + d + \delta y)^2}$
$Fx =$	$\frac{109675.0}{\left(x + f + \frac{\varphi}{x^2}\right)^2}$	$\frac{109675.0}{\left(x + f + \frac{\varphi}{x}\right)^2}$	$\frac{109675.0}{(x + f + \varphi y)^2}$

“Also it shows conclusively that such difference cannot be 0,5, a supposition, which has suggested the idea that the  $P$  and  $S$  are similar series,  $P$  with even numbers and  $S$  with odd”.

About the  $Fx$  we may remark that  $f$  differs very little from a whole number, and that  $\varphi$  becomes practically equal to zero. So the denominators differ very little from  $3^2$ ,  $4^2$ , etc.

After we have ascertained this, the designation of every spectral line is self-evident. We must, namely express in the designation, of what two terms of what two series its frequency is the difference. So the second line of the principal series is represented by  $S_1 - P_2$ , the whole principal series by  $S_1 - Px$ . So we may omit the sign — for simplicity, and write  $S_1 P_2$  resp.  $S_1 Px$ .

A priori the following series are possible:

I	II	III	IV
<b>Pz Px</b>	<b>Pz Sx</b>	<b>Pz Dx</b>	<b>Pz Fx</b>
<b>Sz Px</b>	<b>Sz Sx</b>	<b>Sz Dx</b>	<b>Sz Fx</b>
<b>Dz Px</b>	<b>Dz Sx</b>	<b>Dz Dx</b>	<b>Dz Fx</b>
<b>Fz Px</b>	<b>Fz Sx</b>	<b>Fz Dx</b>	<b>Fz Fx</b>

Up to now only one or more lines have been observed of the series printed in big type.

The series in column I we call *Principal series*. They form together a group of *Translation series* (cf. p. 157), and differ only in asymptote.

<sup>1)</sup> l. c. p. 77.

As asymptotes are known up to now  $P_1$  and  $S_1$ , which both also occur in the Natrium system, which has been drawn on the adjoined plate. To the *Sharp series*, as we shall call all the series belonging to column II, the same thing applies. They too form a translation group, in which  $P_1$ ,  $P_2$ , and  $P_3$ , occur as asymptotes, with all three of which we meet again also for the Natrium. The translation group of the Diffuse series, which all belong to column III has as asymptotes:  $P_1$ ,  $P_2$ ,  $P_3$ ,  $S_1$ , and  $S_3$ , the four first-mentioned of which occur in the Na-spectrum. Column IV contains the *Fundamental series*, which have as asymptotes  $P_1$ ,  $S_1$ ,  $D_1$ ,  $D_2$  and  $F_5$ . Only  $P_1$ ,  $D_1$  and  $F_5$  occur in the Natrium spectrum.

In case one should object to the names of Diffuse and Sharp Series, because not all the lines of all the diffuse series are diffuse, and not all those of all the sharp series are sharp, we may also simply speak of *D-* resp. *S-*series. In this connection I will quote an expression of Hicks<sup>1)</sup>:

“Regarded from this point of view, we may look upon *P* as standing for positive, *D* for difference and *S* for semi”.

To make clear the connection between the old and the new names, this table may serve: (see p. 161).

If a series is composed of several components, they may be distinguished by accents, e. g.  $P_1 D_x$ ,  $P_1' D_x$ ,  $P_1'' D_x$ . In this it is worthy of note that the different components of the *S-*, *D-*, and *F-*series resp. belong to the same translation group. Only for the *P-*series it is slightly different. There the asymptote remains the same, but the curve for the two components has a somewhat different position. So  $S_1 P_x$ , which denotes the 2<sup>nd</sup> component of the principal series, belongs to the same translation group as  $P_1' P_x$ , which group however, differs somewhat from that of the *P-*series. They occur both also for Natrium, but have been omitted on the plate for clearness' sake.

If we examine this plate, we notice first of all, that *all the recorded curves were drawn off* the same pattern curve, which consists of a thick brass plate, into which according to my data the curve:

$$y = \frac{109675.0}{x^2}$$

has been incised in an exceedingly careful way, so that  $x = 1$  is represented by a distance of 4 c.m., while  $y = 10^8 \lambda^{-1}$  ( $\lambda$  expressed in Å.U.) has been taken so that 1 m.m. corresponds to a frequency 100. The other sides of the templet constitute the two axes of the system, on which the curve has been drawn. Both sides are provided with a

<sup>1)</sup> l. c. p. 96.

New appellation	Symbol	Old appellation or symbol <sup>1)</sup>
Principal series (P-series)	$P_1 Px$	Comb <sup>2)</sup> : $2p - 3p; 2p - 4p; 2p - 5p; 2p - 6p; \text{etc.}$
	$S_1 Px$	Principal series.
Sharp series (S-series)	$P_1 Sx$	2nd Subordinate series.
	$P_2 Sx$	Comb: $3p - 1.5s; 3p - 2.5s; 3p - 3.5s.$
	$P_3 Sx$	Comb: $4p - 2.5s; 4p - 3.5s.$
Diffuse series (D-series)	$P_1 Dx$	1st Subordinate series.
	$P_2 Dx$	Comb: $3p - 4d; 3p - 5d; 3p - 6d.$
	$P_3 Dx$	Comb: $4p - 4d; 4p - 5d.$
	$S_1 Dx$	Comb: $1.5s - 3d; 1.5s - 4d; 1.5s - 5d; 1.5s - 6d.$
	$S_3 Dx$	Comb: $3.5s - 3d.$
Fundamental series (F-series)	$P_1 Fx$	Comb: $2p - 4 \angle p; 2p - 5 \angle p; 2p - 6 \angle p$
	$S_1 Fx$	Comb: $1.5s - 6 \angle p.$
	$D_1 Fx$	Bergmann series.
	$D_2 Fx$	Comb: $4d - 4 \angle p; 4d - 5 \angle p.$
	$F_3 Fx$	Comb: $\frac{N}{5^3} - 4 \angle p; \frac{N}{5^2} - \frac{N}{6^2}.$

vernier one of which corresponds with a division in mm. on a brass ruler 1 m. long (to be used along the  $y$ -axis), and the other with a division in  $0,1 x (= 4 \text{ mm.})$  on a rectangle also of brass for the asymptotes. Everything has been executed with the utmost care in the Factory of Scientific Instruments, P. J. KIPP and Sons, J. W. GILTAY succ. Delft.

On the plate we find a system of axes  $OXYZ$ , and the  $YOZ$ -plane is turned over to the left. Here the curves:

$$y = Fz, \quad y = Pz, \quad y = Sz \quad \text{and} \quad y = Dz$$

have been drawn.

All the  $F$ -curves and  $F$ -asymptotes have been indicated by \_\_\_\_\_

„ „  $P$  „ „  $P$  „ „ „ „ „ „ ————  
 „ „  $S$  „ „  $S$  „ „ „ „ „ „ —·—·—·—·—·—·—  
 „ „  $D$  „ „  $D$  „ „ „ „ „ „ —·—·—·—·—·—·—

<sup>1)</sup> Cf. Dunz. l.c.

<sup>2)</sup> This series was called third subordinate series by SAUNDERS before. Proc. Amer. Acad. 40, p. 439, 1904.

The four mentioned curves are all four the same, but each in another position. For  $z=1.2.3$  the curve  $y=Pz$ , yields the values  $P_1, P_2, P_3$ , which indicate three  $P$ -asymptotes (— — —) in the  $YOX$ -plane. In the same way the  $S_1$ -asymptote (— . . . —), the  $D_1$ -asymptote (— . . . —) and the  $F_5$ -asymptote (—) is obtained. In other spectra  $D_2, S_3$  etc. can also appear as asymptotes. We now find the following curves in the  $YOX$ -plane, in which I have now once more given the meaning in the new and the old nomenclature.

$y = S_1 P_x$	Principal	series with $S_1$ -asymptote.	Principal series.
$y = P_1 S_x$	Sharp	„ „ $P_1$	2 <sup>nd</sup> Subordin. series.
$y = P_1 D_x$	Diffuse	„ „ $P_1$	1 <sup>st</sup> „ „
$y = P_1 P_x$	Principal	„ „ $P_1$	3 <sup>rd</sup> „ „
$y = P_1 F_x$	Fundamental	„ „ $P_1$	Comb : $2p - m\Delta p$ .
$y = P_2 S_x$	Sharp	„ „ $P_2$	Comb : $3p - ms$ .
$y = P_2 D_x$	Diffuse	„ „ $P_2$	Comb : $3p - md$ .
$y = P_3 S_x$	Sharp	„ „ $P_3$	Comb : $4p - ms$ .
$y = P_3 D_x$	Diffuse	„ „ $P_3$	Comb : $4p - md$ .
$y = D_1 F_x$	Fundamental	„ „ $D_1$	Bergmann series.
$y = F_5 F_x$	Fundamental	„ „ $F_5$	Comb : $\frac{N}{5^2} - m\Delta p$ ,

and further the curve  $y = oF_x$ , so this is the original curve on its original system of axes.

In the above table I have arranged the curves according to their asymptotes. We can now also easily arrange them in Translation groups.

$y = S_1 P_x$ and $y = P_1 P_x$	form together the Translation group	$P$
$y = P_1 S_x; y = P_2 S_x; y = P_3 S_x$	„ „ „ „ „	$S$
$y = P_1 D_x; y = P_2 D_x; y = P_3 D_x$	„ „ „ „ „	$D$
$y = P_1 F_x; y = D_1 F_x; y = F_5 F_x$	„ „ „ „ „	$F$

*All the curves representing series which belong to one and the same Translation group, have been indicated in the same way, so:*

All the members of the Translation group	$P$	by	— — —
„ „ „ „ „ „ „ „	$S$	„	— . . . —
„ „ „ „ „ „ „ „	$D$	„	— . . . — . . . —
„ „ „ „ „ „ „ „	$F$	„	—————

*All the curves indicated in the same way can be made to cover each other by merely a translation //  $Y$ -axis.*

If we wish to make a spacial representation of the whole system of series, we need only think the  $YOZ$ -plane rotated back to its original position, then the different curves will lie in different planes



// $YOX$ -plane. All the series with asymptotes  $P_1 S_1 D_1$  then get into the plane  $z = 1$ , those with asymptotes  $P_2, D_2$  etc. in the plane  $z = 2$  etc.

By means of this plate we can now easily demonstrate, how the whole system may be built up, when only some spectral lines are known.

Let us suppose e.g. that 3 lines of the  $P$  series with  $S_1$  asymptote  $S_1 P_x$  or Principal series have been observed, then the curve  $Y = S_1 P_x$  can be drawn in the  $YOX$ -plane and the curve  $Y = P_z$  in the  $YOZ$ -plane. The latter yields for  $z = 1$  the asymptotes  $P_1, P_2, P_3$ , which may be drawn in the  $YOX$ -plane.  $S_1$  and  $P_1$  being known, the  $S$  series with  $P_1$  asymptote ( $P_1 S_x$  or 2<sup>nd</sup> subordinate series) is given for the greater part (i.e. without the rotation). If one more line is known of this series, the curve  $Y = P_1 S_x$  is perfectly determined, and so also the curve  $Y = P_2 S_x$  and  $Y = P_3 S_x$ . If we now draw the curve  $Y = S_x$  in the  $YOZ$ -plane, the former yields at once the asymptotes  $S_1, S_2$  etc.

If one line is known of a Diffuse series, e.g. that with  $P_1$  asymptote ( $P_1 D_x$  or 1<sup>st</sup> subordinate series), then the curve  $Y = P_1 D_x$  may be drawn in its main-features (so without rotation), and it is perfectly determined by a second line. So all the  $D$  series are known, and all the  $D$  asymptotes may be found by drawing the curve  $Y = D_z$  in the  $YOZ$ -plane. Now all the asymptotes of the Fundamental series are known, so they may all be drawn *without it being necessary that one knows one line of it by observation*. So the whole system of series is known through six lines, provided only one component be used, as has been expressly stated. We draw attention to the fact, that this is possible only by the idea of unity, by which we are guided:

For all the series the curve by which they may be denoted in the indicated way, is *the same*.

Besides the easy survey of the whole system of series and the well-arranged whole, which we owe to this way of considering the matter, our plate can teach us several things more.

It shows us in what region there are still lines wanting in the spectrum, and where endeavours to find new lines have a great chance of success.

Reversely, if new lines have been found from the experiments in a certain spectral region we can by marking their frequencies on the  $Y$ -axis and by drawing lines //  $X$ -axis, determine the points of intersection of these lines and the traced curves, and see which of these points of intersection then coincide with the lines  $x = 1 . 2 . 3$ .

etc. We know then at once to what series they belong, and so what place they occupy in the whole system. If a meeting as discussed above should not take place for a line, we should consider that the line may belong to a series for which no other member has been found as yet for *that* element. Then the whole system of asymptotes ( $P_1, P_2 \dots, S_1, S_2 \dots D_1, D_2 \dots F_1, F_2 \dots$ ) should be drawn, after which the templet should be made to run successively along these asymptotes, in which way it is easy to find to what asymptote the considered line belongs. From the  $X$ -translation, which the templet then has, one can derive at once to what translation group the series belongs. In this way our pattern curve can be very serviceable in detecting and arranging new lines.

I should like to draw attention to another point. When we draw the systems of series for the different elements (I have, of course, only been able to select one for the adjoined plate), all kinds of different types are found. Gradual changes take place when we proceed from one element to another in the same column of the table of MENDELEJEFF, and also when we pass on to the other columns, the occurring changes in the type are very great. I hope to publish the results of a more extensive study on these changes later on. I will make some remarks about this already here. On the annexed plate we find e.g. the asymptote  $S_1$  of the  $P$  series lying *above* the  $P_1$  asymptote of the  $S$  and  $D$  series. We also see that  $S_1 P_1$  is *pos.* and  $P_1 S_1$  *neg.* for  $x = 1$ . The absolute value of the two ordinates is the same.

We find the same behaviour in the systems for the other alkali-metals, and also  $H$ ,  $He$ , and  $O$ . If we compare this with a diagram of the Thallium system or some other heavy metal, we observe exactly the reverse. Now the  $S_1$  asymptote of the  $P$  series lies *under* the  $P_1$  and  $P_1'$  asymptotes of the two components of the  $S$  and  $D$  series. Moreover  $S_1 P_1$  and  $S_1 P_1'$  are now *negative* and  $P_1 S_1$  and  $P_1' S_1$  are the same, but *positive*. I will not enter just now into other points of difference between the two types. I will only draw attention to the following points:

As appears from the diagram, the *negative frequencies* naturally occur here. So, as we are here almost compelled by the principle of continuity, to assume negative frequencies, I consider the objections, entertained by MOGENDORFF <sup>1)</sup> against formulae with negative frequencies, entirely unfounded.

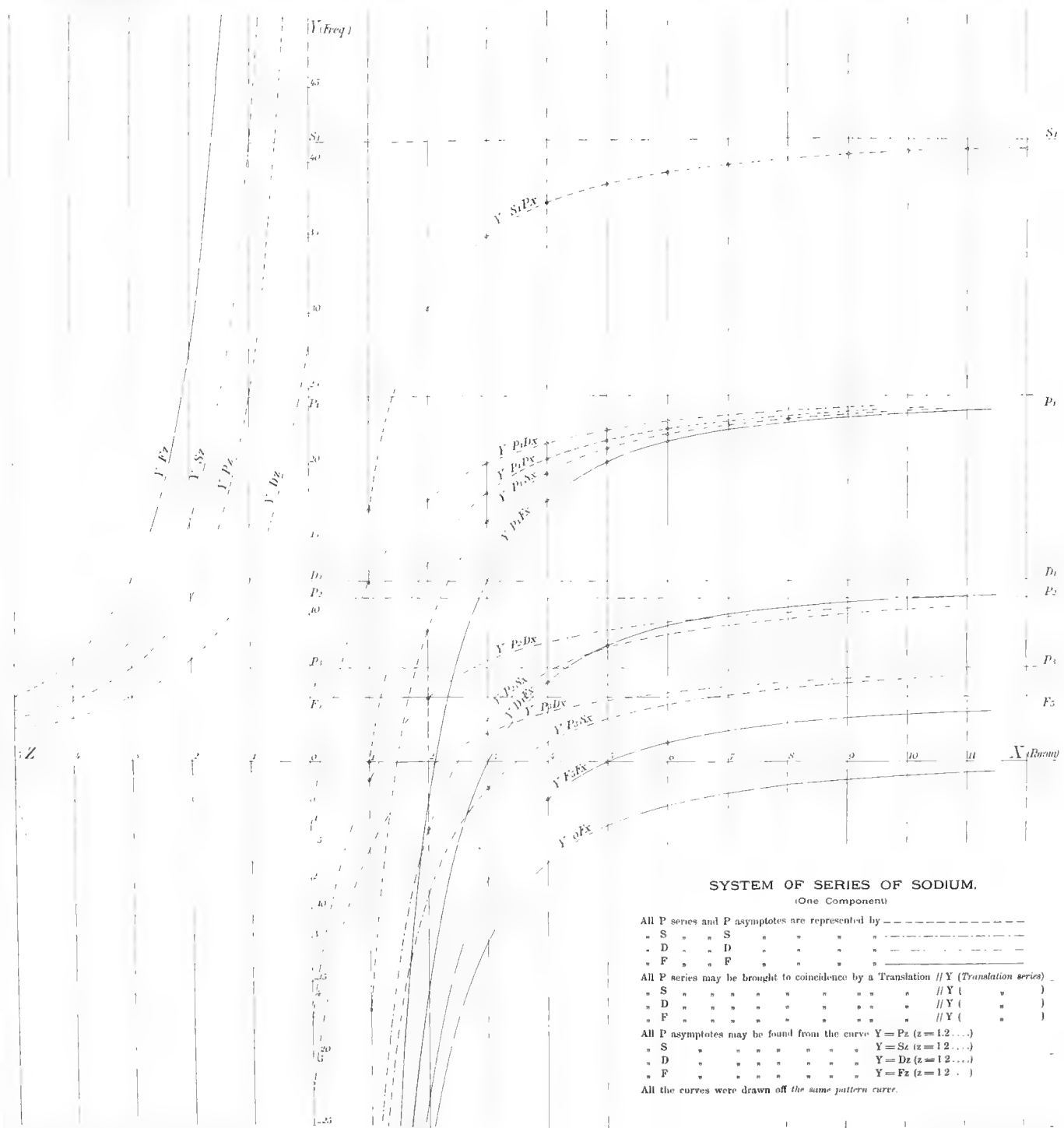
In the same way the objection that MOGENDORFF <sup>2)</sup> advances to the

<sup>1)</sup> Thesis for the doctorate, Amsterdam, p. 39.

<sup>2)</sup> loc. cit. p. 39.

*TV*





**SYSTEM OF SERIES OF SODIUM.**  
(One Component)

All P series and P asymptotes are represented by ————

- S     "    S     "    "    "    "    "    "    "    "    "    "    "    "    "
- D     "    D     "    "    "    "    "    "    "    "    "    "    "    "
- F     "    F     "    "    "    "    "    "    "    "    "    "    "    "

All P series may be brought to coincidence by a Translation // Y (Translation series)

- S     "    "    "    "    "    "    "    "    "    "    "    "    "    "    "
- D     "    "    "    "    "    "    "    "    "    "    "    "    "    "
- F     "    "    "    "    "    "    "    "    "    "    "    "    "    "

All P asymptotes may be found from the curve  $Y = Pz$  ( $z = 1, 2, \dots$ )

- S     "    "    "    "    "    "    "    "    "    "    "    "    "    "
- D     "    "    "    "    "    "    "    "    "    "    "    "    "    "
- F     "    "    "    "    "    "    "    "    "    "    "    "    "    "

All the curves were drawn off the same pattern curve.

formula of RITZ that the succession of the lines is irregular, is quite removed by the introduction of the negative frequencies and the continuity obtained through it.

Further our plate of the Natrium system throws light on the so-called summational and differential series, discussed by MOGENDORFF<sup>1)</sup>. We find two  $P$ -series in the spectrum of Na; viz.  $P_1 Px$  and  $S_1 Px$ . The corresponding terms of the two series show the constant difference of frequency  $S_1 P_1$ , which also represents the frequency of the first term of the  $P$  series with  $S_1$  asymptote.

According to MOGENDORFF<sup>2)</sup> the series  $P_1 Px$  is now a differential series of  $S_1 Px$  and  $S_1 P_1$ , or as we may briefly write:

$$S_1 Px - S_1 P_1 = P_1 Px.$$

Such a relation can also be easily shown between other translation series e. g.

$$P_1 Dx - P_1 P_2 = P_2 Dx.$$

Here it are the two  $D$  series:  $P_1 Dx$  and  $P_2 Dx$ , of which the corresponding terms show the constant difference in frequency which exists between their asymptotes, viz.  $P_1 P_2$ , which is also the 2<sup>nd</sup> term of  $P_1 Px$ ; according to MOGENDORFF the 1<sup>st</sup> line of the differential series. As appears from the plate, however, (the observed lines are indicated by 0), this line has not yet been observed, though it (2 7510) lies in a region very well accessible to observation. So it will probably have a very slight intensity. That this line would give rise to a whole series of differential vibrations, seems, indeed, somewhat strange to me. From the asymptotes of one Translation group we can write all kinds of constant differences of frequency, for which a line is often to be found then. In this way we can indicate the members of one Translation group in all kinds of ways as summational and differential series. So we get simply here RITZ's "Kombinationsprinzip", in somewhat modified form, for which PASCHEN<sup>3)</sup> has already given a scheme for the Potassium spectrum, according to which scheme DUNZ<sup>4)</sup> has calculated the systems of series for different elements. These systems, however, share the drawback of MOGENDORFF's system of being confusing and difficult to survey, which drawback is entirely removed by the introduction of the Translation series.

<sup>1)</sup> Summational and differential vibrations in line spectra. Proc. Kon. Akad. v. Wet. Amsterdam. 25 November 1911 p. 470.

<sup>2)</sup> l. c. p. 474.

<sup>3)</sup> Jahrbuch der Radioaktivität und Elektronik Bd 8 p. 174. 1911.

<sup>4)</sup> l. c. p. 39.

**Chemistry.** — “*Determinations of the vapour tension of nitrogen tetroxide*”. By Dr. F. E. C. SCHEFFER and J. P. TREUB. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of May 25, 1912).

1. In a previous treatise<sup>1)</sup> we communicated the results of an inquiry into the vapour tensions of nitrogen tetroxide. In these determinations we made use of a method which had been applied before by different investigators (LADENBURG, RAMSAY and YOUNG, BODENSTEIN, JOHNSON and JACKSON) in measurements of vapour tensions of substances which could not be brought into contact with mercury. Of the forms of the manometer proposed by the said investigators we chose that described by JACKSON, because this manometer can be very easily constructed, and the accuracy which we wanted to reach, can be easily obtained by means of this apparatus. Moreover by means of this manometer it seemed possible to us to devise a method to determine the vapour pressures of substances attacking mercury up to the critical pressure. As a sequel to the determinations to three atmospheres given in the preceding paper, we shall give a description here of this method for higher pressure, and state the results which make the vapour tension line of the nitrogen tetroxide up to the critical temperature known to us.

2. *Critical temperature.* Before entering upon the description of the vapour tension determinations at higher pressure, we will first mention a determination of the critical temperature, which we did not carry out with the measurements of the vapour tension, but in another way independent of these. A thickwalled tube of combustion glass provided with a capillary constriction was connected by means of a ground glass junction with the reservoir with nitrogen tetroxide. After the tube had been evacuated by means of the GAEDE-pump (with cooling of the nitrogen tetroxide with a carbonic acid alcohol mixture), and the connection with the pump had been melted off, the tube was filled by the liquid being distilled over, so that the liquid took up a volume that was somewhat smaller than half that of the tube. Then the latter was melted off at the capillary constriction, and heated in a bath of paraffin oil.

The liquid, which is almost colourless in the neighbourhood of

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<sup>1)</sup> These Proc. Vol. 14, p. 536.

the melting-point, and has a yellow brownish colour at the temperature of the room, becomes darker with rise of temperature; at about  $50^{\circ}$  it is already dark brown, and the transparency diminishes gradually with ascending temperature. The vapour which has a lighter colour at equal temperature on account of its slighter density, also gets darker with increasing temperature, so that above  $100^{\circ}$  the meniscus between liquid and vapour can hardly be distinguished. Hence the critical phenomenon of this darkbrown liquid and vapour has not been directly observed. The only value of the critical temperature recorded in the literature, has, accordingly, not been determined by an optical, but by another way.

For the determination of the critical temperature NADEJDINE <sup>1)</sup> made use of a very ingenious method, which, however, has not yielded accurate results. A tube was provided with a balance-knife in the middle so that it could execute regular oscillations round the state of equilibrium. If now the tube is filled with nitrogen tetroxide, regular oscillations are impossible, the tube inclines to the side where the liquid is. With rise of temperature above the critical however, the tube fills homogeneously, and gets in equilibrium. The temperature, at which this setting in of the equilibrium takes place, was considered to be the critical temperature; it amounted to  $171,2^{\circ}$  C.

We have, however, succeeded in observing the critical phenomenon directly optically. With incident and transmitted light there is nothing to be observed of the critical phenomenon in our tubes of about 3 mm. bore (thickness of the wall 3 mm.). Even the use of an arc lamp did not bring a change. When, however, we threw the light on the tube (in a bath of paraffin oil), and directed our eye so that the light that was reflected on the inner wall of the tube, could reach our eye, we could clearly distinguish the demarcation between liquid and vapour. In one of the tubes we saw the meniscus quickly shift to one of the extremities on rise of temperature, and disappear suddenly. In another tube, the volume of which pretty well agreed with the critical volume of the filling, the line of demarcation disappeared suddenly about in the middle of the tube. Both tubes yielded  $158,2^{\circ}$  C. for the temperature at which the demarcation between liquid and vapour disappeared. We have repeatedly carried out these determinations independently of each other; the obtained values agreed within  $0,2^{\circ}$ . So the critical temperature amounts to  $158,2^{\circ}$ , and accordingly differs considerably from the value given by NADEJDINE.

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<sup>1)</sup> Beibl. 9, 721 (1885).

3. *The vapour tension determinations.* The apparatus used by us for the vapour tension determinations, is represented in fig. 1.

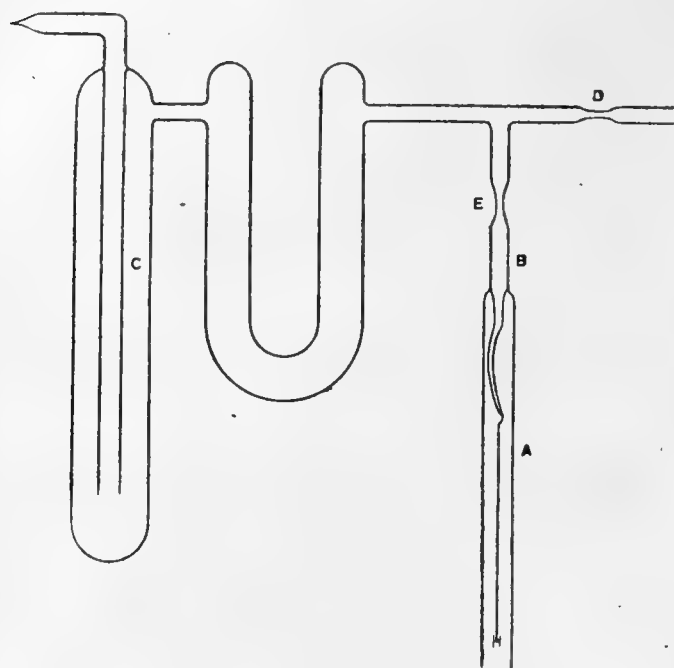


Fig. 1.

The manometer, which is fused into the tube *A*, differs from the one described in our previous communication only in this that it is more elongated and smaller; the length of the curved part amounts to three or four cm., while the tube *A* has an external diameter of 10 mm. and a length of 22 or 23 cm. The entire apparatus serving for the measurements has a length of about 28 cm. after the constriction at *E* has been

melted off. On the outer tube *A* two marks have been made, so that the end of the needle is just between the two marks when the internal and external pressure is the same. The manometer can resist an excess of pressure of one atmosphere, and can therefore be evacuated; then the end of the needle reaches the inner wall of *A* in some of the apparatus used by us. The sensitivity reached with this shape of apparatus varies between  $\frac{1}{20}$  and  $\frac{1}{10}$  atmosphere.

Before the apparatus was filled the reservoir *C* with the nitrogen tetroxide was cooled by means of a mixture of carbonic acid-alcohol, and evacuated by means of a GAEBDE-pump through *D*. Then the constriction *D* was melted off, and a quantity of nitrogen tetroxide was distilled over through the *U*-tube with phosphorus-pentoxide into *B*; for this purpose a cylindrical vessel was placed round the tube *A* by means of a cork, which vessel could be filled with alcohol cooled by carbonic acid. When a sufficient quantity of liquid was distilled over, the apparatus was separated from the filling apparatus by melting off at *E*, after the nitrogen tetroxide in *B* and *C* had been brought to  $-80^{\circ}$ .

We have applied two different methods for the determination of vapour tensions.

*a.* For our first determinations we made use of the arrangement indicated in Fig. 2*a*. The apparatus *AB* was slid into a thickwalled combustion tube, so that it rested on the constriction at *C* with a copper spiral, which is not drawn in the figure. At the lower end of the combustion tube a combustion capillary *D* of 3 mm. bore



and with a wall of 3 mm. thickness was fused to the apparatus, which was cemented into a mounting for CAILLETET experiments. The upper end of the combustion tube was fused to by means of an oxygen gas flame. After evacuation with a water-jet pump the combustion tube was filled with a glycerin-water mixture, and screwed into a CAILLETET-pressure-cylindre filled with the same liquid. Then a cylindrical glass jacket was put round the combustion tube by means of a rubber stopper prepared for high temperatures, in which jacket different liquids were electrically heated under varying pressure till they boiled (by means of the heating wire wrapped

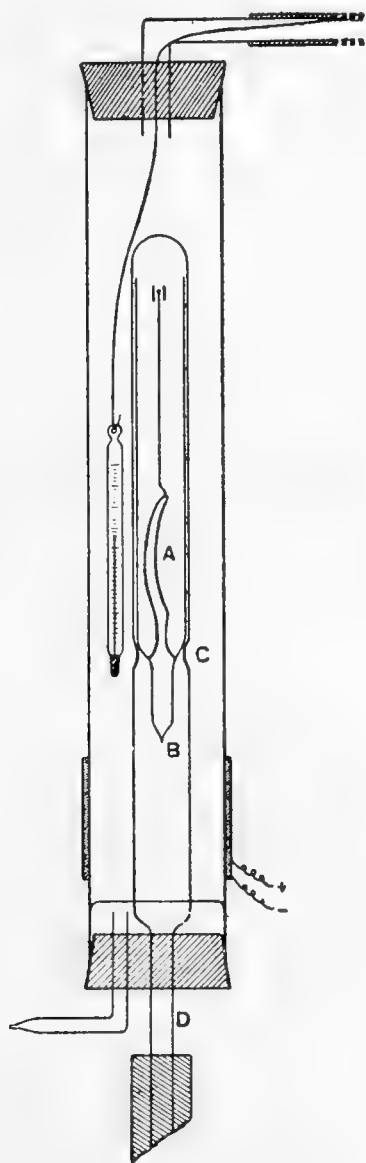


Fig. 2a.

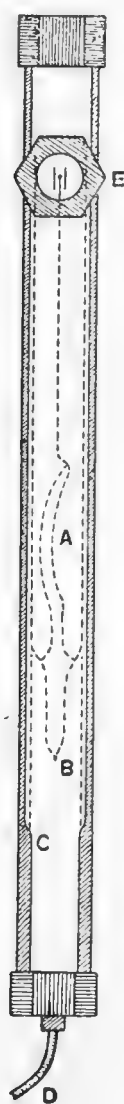


Fig. 2b.

round the tube and drawn in fig. 2a). The rubber stopper was protected against the action of the boiling liquid by a layer of mercury. The condensation ring of the boiling liquid was always raised to above the extremity of the combustion tube, the temperature was

read on an Anschützthermometer (which had been compared with a normal thermometer) the mercury bulb of which was at a level with the nitrogen tetroxide.

For the determination of the pressure this was regulated by means of a CAILLETET-pump in such a way that the needle was exactly between the marks on the tube *A*, and read on a SCHÄFFER and BUDENBERG metal manometer gauged by means of a pressure-balance. The liquids which we have used for heating, were successively alcohol, toluene, xylol, and aniline; the bumping was prevented by a stream of air-bubbles, which were sucked in through the tube that passed through the stopper.

The results obtained by this method, will be described in § 4. The experiments arranged in this way always finished up with an explosion; the highest pressure we reached was 67 atmospheres. The critical pressure, however, lying higher, we were obliged to have recourse to another method for the determination of the higher vapour-tensions.

*b.* In our further experiments we abandoned the use of a combustion tube, and replaced it by a copper tube. In this we had first of all to face the difficulty to arrange it in such a way that the reading of the position of the manometer needle was possible. For this purpose near the end of the tube two transverse tubes were adjusted, which could be closed by means of perforated screws, one of which (*E*) has been drawn in fig. 2*b*. The hole through these screws was closed with a glass plate, which was pressed to the tube by the screw. To make this arrangement tight at high pressure was at first attended with great difficulties. We tried to reach this by screwing the glass plates to the tube between rings of leather; it was, however, impossible to get a sufficient closure in this way.

Then we pressed the plates between plaster of Paris, and between copper, made soft by being made red-hot, always, however, with a negative result. After these futile attempts we cemented the plates in loose steel mountings, and screwed these mountings with copper plates into the tube. As cement we tried first a mixture of soluble glass, zinc oxide, and magnesium oxide; once we succeeded in this way to obtain a sufficient closure up to 100 atmospheres, generally, however, the soluble glass showed cracks, which allowed the liquid in the copper tube to get through on increase of pressure. At last we succeeded in cementing the glass plates into the steel mounting by means of an enamel obtained by melting from sodium- and potassium carbonate, silicium oxide, and lead oxide. By heating with a Tecluburner this enamel melted, and entirely filled the narrow opening between

glass and steel, and continued to close after it had been cooled, up to a pressure of 150 atmospheres.

Now the apparatus *AB* was slid into the tube; it rested on the constriction *C* by means of a loose glass tube that tightly fitted in the copper tube; the length of this tube was chosen so that the end of the manometer needle was exactly between the two glass plates in the holes in the screws, so that it was possible to read the position with an incandescent lamp placed behind it. The narrow copper tube *D*, which formed the connection with the CAILLETET-pump, was fastened to the lower end of the copper tube by means of a screw. Now the tube was quite filled with the glycerin water solution, and closed at the top with a screw.

So in this way we had obtained an arrangement which could resist pressures of about 150 atmospheres. It only remained to us to find a method to heat this copper tube to varying temperatures.

We have tried to use an oil-bath for the heating, and to place the tube in the bath in such a way that the end in which the glass plates were, projected above the bath. This was required for the accurate reading of the needle, and to have at the same time an opportunity to clean the glass panes when in course of time the screws began to leak a little in consequence of the increase of temperature. This method of heating, however, appeared to give unreliable results in spite of different modifications. It appeared that the part that projected above the liquid caused a loss of heat, so that the temperature of the nitrogen tetroxide remained lower than the temperature in the oil-bath, so that at a definite temperature always too low pressures were found compared with the results according to the method *a*.

At last we were more successful with another quite different method of heating. The copper tube was quite surrounded by two tightly fitting spirals of hard lead. Through both these spirals an oil-stream was passed, so that the two streams ran in opposite directions; one stream flowed spirally round the tube from below upwards, the other in the opposite direction. The oil-stream was obtained by means of a rotating pump worked by an electromotor, which pressed the oil from a pan heated by two Tecluburners through the spirals. The tube and the heating-spirals surrounding it were first enveloped with thick asbestos cord, and then with a thick layer of cotton waste to prevent emission of heat as much as possible; the inlet and exit tubes were isolated in the same way.

The temperature was read on an Anschütz thermometer, which was placed between the spirals and the tube and of which the part

of the scale that was to be read, was placed behind an opening in the isolation material. Besides this thermometer opening only two small apertures were made in the isolation layer, through which the two small panes remained visible.

4. *Results.* The results obtained by the methods described in the preceding paragraph, have been collected in Table I. They have been made with five apparatus; the determinations in the neighbourhood of the critical temperature have been carried out with an apparatus which was about half filled with liquid at the ordinary temperature, and the volume of which was therefore somewhat smaller than the critical volume. From our determinations at the temperatures in the immediate neighbourhood of  $T_k$  we have determined the critical pressure graphically. The extrapolation that is required for it, can certainly be executed within the error of one atmosphere. Yet we think that we must consider the critical pressure accurate up to two atmospheres. We have namely no perfect certainty that the observations at the highest temperatures refer to the heterogeneous equilibrium. The possibility cannot be entirely excluded that these observations represent a line in the homogeneous liquid region, though these determinations yield a practically continuously progressing curve with those at lower temperatures; if this should be the case, the deviation from the real vapour-tension curve is so slight, that the accurate value of the critical pressure could only be found by means of an extrapolation formula, drawn up from observations at lower temperature. In this, however, we also meet with difficulties, as then the extrapolation would have to take place over a greater range of temperature; we return to this extrapolation in a following paragraph. So we find 100 atmospheres for the critical pressure, in which we must consider a maximum deviation of two atmospheres possible. It will, moreover, be difficult to reach a greater accuracy, as it will not be possible to observe the critical pressure at the same time with the measurement of the pressure without complicating the arrangement considerably. Besides this would give rise to new experimental difficulties, because the critical phenomenon in itself is so very difficult to observe. A manometer which was filled for about two thirds with liquid, presented a sudden deviation from the vapour tension line at about  $140^\circ$ ; the pressure rose abnormally rapidly (about 6 atm. per degree) with slight rise of temperature, much more rapidly than the vapour tension line, even in the neighbourhood of the critical circumstances. So this apparatus is quite filled with liquid at  $140^\circ$ , and the abnormal rise of pressure was

TABLE I.

$t$	$p$	Method	$t$	$p$	Method
54.25	4.1	$a$ (alcohol)	109.8	26.8	$a$ (xylol)
59.6	4.95	$a$ (alcohol)	110.2	26.8	$b$
64.95	6.1	$a$ (alcohol)	110.3	27.0	$a$ (xylol)
70.1	7.3	$a$ (alcohol)	110.8	27.2	$b$
72.7	8.0	$b$	114.5	30.8	$a$ (xylol)
74.7	8.7	$a$ (alcohol)	115.5	31.3	$a$ (xylol)
78.3	9.7	$a$ (alcohol)	115.7	31.6	$a$ (xylol)
78.3	9.6	$b$	119.2	35.3	$a$ (xylol)
79.7	10.1	$b$	120.0	35.7	$b$
81.7	10.8	$a$ (toluene)	120.5	36.3	$a$ (xylol)
82.7	11.1	$b$	125.35	41.6	$a$ (xylol)
86.7	12.9	$b$	125.5	41.8	$a$ (xylol)
87.1	13.0	$b$	131.1	48.8	$a$ (xylol)
88.5	13.6	$a$ (toluene)	131.5	49.3	$b$
92.3	15.3	$b$	134.9	54.4	$a$ (xylol)
93.7	16.1	$a$ (toluene)	139.1	60.5	$a$ (aniline)
98.15	18.6	$a$ (toluene)	142.6	66.6	$a$ (aniline)
100.7	20.3	$a$ (xylol)	142.9	66.4	$b$
100.9	20.3	$a$ (xylol)	151.2	82.4	$b$
101.45	20.5	$b$	152.4	84.5	$b$
101.6	20.7	$a$ (toluene)	156.2	93.6	$b$
104.5	22.6	$a$ (toluene)	157.4	97.2	$b$
105.6	23.3	$a$ (xylol)	$T_k$ 158.2	$P_k$ 100	extrapolation
105.9	23.7	$a$ (xylol)			

therefore owing to the heating of the homogeneous liquid at constant volume.

With every determination in Table I the method used for the observation is given; the pressures are given in atmospheres. In the first four determinations and in the sixth the pressure was not determined by means of a SCHÄFFER and BUDENBERG manometer, but with an air-manometer (air-isotherm of AMAGAT).

It will be clear from the table and the corresponding graphical representation (fig. 3) that there is sufficient harmony between the results obtained by the two methods of observation.

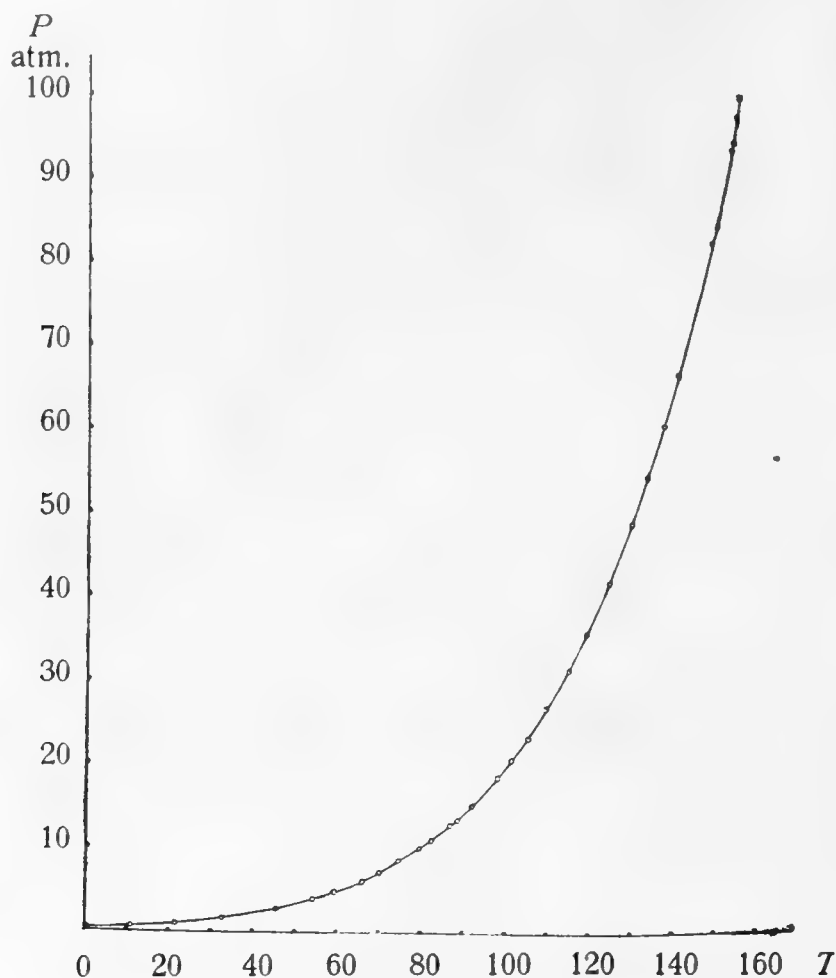


Fig. 3.

By way of control of the pressure measurements we have exposed one of our manometer tubes, after being opened, in the copper tube to the same pressures and temperatures as occurred in our determinations. Then it appeared that in none of the observations a correction was required for a change of the zero position.

5. As for the nitrogen tetroxide we have to do with a substance which is in dissociation, for which the values of the degree of the dissociation appreciably vary both in the liquid state and in the vapour state corresponding with it — for the vapour we already gave some values for the degree of dissociation in our preceding communication — it seemed desirable to calculate the value of  $f$  from VAN DER WAALS'S empirical equation with the aid of our observations. If for this purpose in the equation:

$$-\log \frac{p}{p_k} = f \frac{T_k - T}{T}$$

we substitute the values  $p_k = 100$  and  $T_k = 158.2 + 273 = 431.2$ , our observations yield values of  $f$  varying with the temperature, as will be clear from the subjoined table II.

T A B L E II.

$t$	$T$	$P$	$f$	$t$	$T$	$P$	$f$
7.0	280.0	$\frac{1}{2}$	4.25	100.5	373.5	20	4.5
21.2	294.2	1	4.3	123.8	396.8	40	4.6
46.6	319.6	3	4.35	138.8	411.8	60	[4.7]
79.4	352.4	10	4.5	150.0	423.0	80	[5.0]

The value of  $f$  appears really to reveal the dissociation; it lies, namely, much higher than that of normal substances ( $\pm 3$ ), even higher than that of substances as water and alcohol. It appears at the same time that  $f$  rises with the temperature, whereas the reverse takes place for water and alcohol.

So the inclination of the  $P$ — $T$ -line increases more rapidly with rising temperature than for a normal substance.

In the graphical representation, which occurs in the Theoretische Chemie of Prof. NERNST <sup>1)</sup>, in which  $-\log \frac{p}{p_k}$  is taken as ordinate,

$\frac{T_k}{T} - 1$  as abscissa, nitrogen tetroxide yields therefore a line, which in opposition to that of water and alcohol is concave seen from below, and yields a branch of the fanlike sheaf of lines, which lies still higher than all those indicated in the graphical representation.

We have put the last two values for  $f$  in table II between parentheses, as these change resp. 0.1 and 0.2 by a change of one atmosphere in the value of  $P_k$ , and are therefore distinctly inferior to the preceding ones in accuracy.

6. As appears from the change of colour of liquid and vapour with rising temperature the increase of the degree of dissociation is accompanied by an increase of darkening of the colour according to table IV of our former communication. Hence the supposition naturally suggests itself, that the brown colour is owing to the split molecules, whereas the unsplit molecules are colourless. This supposition has been confirmed by the investigation of SALET <sup>2)</sup>, who has

<sup>1)</sup> p. 237 (1909).

<sup>2)</sup> C. r. 67. 488 (1868).

succeeded in getting quantitative data about the homogeneous equilibrium by a colorimetric method, which data accord well with the determinations from the vapour densities. As the colour of the liquid and the vapour gets darker and darker towards the critical temperature, the degree of dissociation will probably be great at  $T_k$ .

In order to get a criterion about the degree of the dissociation we have calculated the values of  $a$  and  $b$  from the equation of state (as the result of a discussion of one of us with prof. VAN DER WAALS). By substitution of  $T_k = 431.2$  and  $P_k = 100$ , we find:

$$a = \frac{27}{64.273^2} \frac{T_k^2}{P_k} = 0,0105 \text{ and}$$

$$b = \frac{1}{8.273} \frac{T_k}{P_k} = 0,00197.$$

If to get an approximative estimation we now consider the  $b$  as an additive quantity, we can calculate the theoretical  $b$  for  $NO_2$ , resp.  $N_2O_4$  from the tables of the  $b$ -values, and compare them with the values found above.

From the values for nitrogen and oxygen we find in this way for  $NO_2$  and  $N_2O_4$  resp. 0,00226 and 0,00452.

Calculation with the aid of the data about nitrogen oxide and oxygen, resp. nitrogen mon-oxide and oxygen, yields for  $NO_2$  and  $N_2O_4$  0,00186 and 0,00372, resp. 0,00200 and 0,00400.

So we draw the conclusion from these values, that the fluid phase for the critical circumstances consists for by far the greater part of split molecules.

7. The complex behaviour of the nitrogen tetroxide leads us to expect an intricate equation for the  $PT$ -line. Caloric data, which can be of use to us to find the vapour tension equation, are not sufficiently known. For this we must of course know the heat of evaporation and the specific heats along the border-line. The specific heats which are known, refer to unsaturate vapours as far as the vapour state is concerned. Accordingly they would have to be corrected in accordance with the change of the degree of dissociation with the pressure. The heat of dissociation in the homogeneous vapour is known pretty accurately, and so this correction might be applied at those temperatures for which the degree of dissociation in the saturate vapour is known (see preceding communication Table IV). The specific heat of the liquid is almost quite unknown. So even if the heat of evaporation at one temperature were known with sufficient accuracy, the unknown dependence of the specific heats on the



temperature would yet render the drawing up of a formula by the aid of the caloric data impossible.

We will only calculate the value of the heat of evaporation from our vapour-tension determinations by the aid of the equation of CLAPEYRON, which can only be applied for low pressures, because the specific volumes along the border line are unknown at higher pressure. From the equation:

$$T \frac{dP}{dT} = \frac{Q}{V_{gas} - V_l}$$

we find, neglecting  $V_l$  with respect to  $V_{gas}$  and applying the law of BOYLE-GAY-LUSSAC:

$$P V = (1 + x) RT,$$

in which  $x$  represents the degree of dissociation

$$Q = \frac{(1 + x) RT^2}{P} \frac{dP}{dT}.$$

In order to calculate  $\frac{dP}{dT}$  we have represented our determinations at low pressure by an empirical formula. By the aid of the data:  $t = -23, p = 70 \text{ m.M.}; t = 11,0, p = 463 \text{ m.M.}; t = 48.7, p = 2478 \text{ m.M.}$  from our former communication we derive the values  $a = 1325.6$ ,  $b = 3.354$ ,  $c = -0.8950$  for the constants  $a$ ,  $b$ , and  $c$  in the equation:

$$\log p = -\frac{a}{T} + b \log T + c$$

This equation represents our observations of the preceding communication very well. It may be remarked here in passing that this expression can represent the observations at higher pressure even up to about 120' and 36 atmospheres. At higher pressures the curve calculated from the equation deviates slightly towards lower pressure; in the immediate neighbourhood of  $T_k$  the deviations become greater; still even at  $T_k$  the deviation amounts only to about three atmospheres. It is remarkable that this formula drawn up from observations below 3 atmospheres, is able to represent the vapour-tension line of this complicated substance so accurately.

If we now differentiate the obtained expression we find:

$$0,4343 \frac{1}{p} \frac{dp}{dT} = \frac{1325.6}{T^2} + 0.4343 \frac{3.354}{T},$$

which yields after substitution:

$$Q = \frac{1325.6}{0.4343} (1 + x) R + 3.354 (1 + x) RT.$$

If in this expression we substitute the values  $R = 1,985$ ,  $t = 21,2$ , and  $x = 0.15$ , which two last refer to the boiling point, we find for the heat of evaporation at the boiling-point:

9200 calories.

The experimental determinations of BERTHELOT and OGIER<sup>1)</sup> appreciably differ from this value. From a number of values which differ pretty considerably from each other, which, however, all of them lie lower than the above mentioned one, they consider 8600 calories the most probable. We, however, think that we have to prefer our calculation, the more so as the determinations which have served for our calculation, just lie in the temperature region over which RAMSAY and YOUNG's investigation extended, and the determinations of the latter do not practically differ from ours.

In conclusion we wish to avail ourselves of this opportunity to express our thanks to Prof. SMITS for his advice in the experimental difficulties experienced by us, and for the interest shown by him in our work.

*Anorg. Chem. Laboratory of the  
University of Amsterdam.*

**Physics.** — “*Electric double refraction in some artificial clouds and vapours.*” (Third part). By Prof. P. ZEEMAN and C. M. HOOGENBOOM.

18. The results obtained with the sal-ammoniac fog might be explained by postulating the existence of two varieties of sal-ammoniac crystals. This hypothesis was put forward in § 17. In the textbooks on crystallography, which were at the disposition of the authors, nothing however, relating to dimorphism of sal-ammoniac could be found. This seemed rather unfavourable to the proposed explanation. We are much indebted therefore to Dr. F. E. C. SCHEFFER, who gave us some references to the chemical-crystallographical literature, from which it appears that the dimorphism of sal-ammoniac is a well-known fact (see v. GROTH, *Chemische Kristallographie*. Band I. S. 167. 1906).

STAS<sup>2)</sup> while sublimating  $\text{NH}_4\text{Cl}$  had observed a phenomenon closely resembling the transformation of polymorphous substances; he did not try however an explanation and it seems that he did not think of dimorphism.

<sup>1)</sup> *Ann. de Ch. et de Ph.* (5) **30** 398 (1883).

<sup>2)</sup> STAS. *Untersuchungen über die chemischen Proportionen u.s.w. deutsch von Aronstein*. S. 54. Leipzig 1867.

LEHMANN <sup>1)</sup> was the first to suggest that the ammonium salts are dimorphous and he tried to prove it by experiments on crystallization of solutions, containing simultaneously two or three of the three halogenous ammonium salts. His result was: "dass hier ein sehr eigenthümlicher Fall von Dimorphie vorliegt, insofern anzunehmen ist, dass alle drei Körper in je zwei Modificationen krystallisiren, und zwar beide regulär, beide in Würfeln, nur insofern unterschieden, als die der niedrigeren Temperatur entsprechende Modification in salmiakähnlichen Skeletten, die der höheren entsprechende in scharfkantigen vollkommenen Krystallen auftritt."

For our purpose it was of particular interest to know whether the two modifications of sal-ammoniac appear also after sublimation. As will be proved below (see § 19) all the phenomena which we described (§ 14, 15, 16) can be obtained with sublimated sal-ammoniac also; the transition of one modification to the other one might then be accompanied with a change of the sign of the electric double refraction.

In this connection an investigation of GOSSNER <sup>2)</sup> merits our attention. GOSSNER among other things repeats an experiment of STAS and we may be permitted to give here his description:

"Im Gegensatze zu LEHMANN hält RETGERS <sup>3)</sup> die Dimorphie der Ammoniumhalogenide nicht für bewiesen. STAS's Beobachtungen entsprechen zwar ganz den Vorgängen, die bei polymorphen Umwandlungen zu beobachten sind, doch erklärt STAS selbst die Erscheinung nicht durch Dimorphie. Nachdem mancherlei Krystallisationsversuche zur Entscheidung der Frage ob der Salmiak dimorph wäre ohne Resultat verliefen, wurde der Versuch von STAS in ähnlicher Weise wiederholt. In ein 2.8 c.M. weites Glasrohr von 70 c.M. Länge das am einem Ende verschlossen war, wurde ein ca. 15 c.M. lange Schicht Salmiak gebracht, der durch Sublimiren vollständig getrocknet und gereinigt war. Die Schicht war nach dem offenen Ende zu mit Glaswolle abgeschlossen, da die Beobachtung ergeben hatte, dass beim Sublimiren im Vacuum feste Salmiakteilchen mitgerissen wurden. Das vordere offene Ende wurde in eine enge Röhre ausgezogen, mit der Saugpumpe in Verbindung gesetzt. Der leere Theil der Röhre wurde dann unter fortwährendem Saugen circa zwei Stunden lang schwach erhitzt um alle Salmiak Keime daraus zu vertreiben. Als sodann bei

<sup>1)</sup> Zeitschr. f. Krystallographie 10. 321. 1885.

<sup>2)</sup> GOSSNER, Zeitschr. für Krystallographie u. Mineralogie herausgegeben von GROTH. 38. 128. 1903.

<sup>3)</sup> ARZRUNI, Die Beziehung zwischen Krystallform u. s. w.; in GRAHAM-OTTO'S Lehrbuch der Chemie 1898. 1 (3). 321. 3 Aufl.

einem Drucke von 15 mm. die Salmiakschicht langsam erwärmt wurde, sublimirte  $\text{NH}_4\text{Cl}$  in den leeren Raum und setzte sich in winzigen lebhaft glänzenden Kryställchen, die allmählich zu einem dicken Ringe sich vermehrten, an den Glaswänden ab. Die Kryställchen erwiesen sich im parallelen polarisirten Lichte als einfachbrechend. Doch war eine genauere Beobachtung über Krystallform und Ausbildung nicht möglich. Bei Unterbrechung des Versuches begann plötzlich der Ring vom kälteren Ende aus sich zu trüben und undurchsichtig zu werden. Die Grenze zwischen der trüben und der sehr lebhaft glänzenden ursprünglichen Partie schritt langsam auf Kosten der letzteren weiter und war dabei scharf zu verfolgen, genau wie bei der Umwandlung eines charakteristisch dimorphen Körpers. Dabei entstanden zahlreiche Risse in der ganzen Masse. Der Vorgang war mit einer bedeutenden Volumenänderung verbunden, was sich durch ein lebhaftes Knistern äusserte, ähnlich wie wenn ein ziemlich starkwandiges Glasrohr zerspringt. Leider war es nicht möglich Kryställchen längere Zeit zu erhalten. Meist traten die eben beschriebenen umwandlungsartigen Erscheinungen schon während des Versuches ein. Immer aber trat die Umwandlung während des Abkühlens ein. Es war deswegen eine physikalische und krystallographische Untersuchung des ersten Sublimationsproductes nicht möglich. Doch besteht zwischen den typischen Umwandlungserscheinungen und den bei diesen Versuchen beobachteten Erscheinungen, wie schon erwähnt eine vollkommene Aehnlichkeit. Es ist daher der Schluss sehr wahrscheinlich gemacht, dass wir es hier mit einer polymorphen Umwandlung zu thun haben und dass das Chlorammonium in zwei Modificationen existirt."

We have verified these results. It appeared, however, that it was unnecessary to produce a vacuum.

After having observed once the transition, experimenting according to STAS' precepts, we had no difficulty in obtaining the phenomenon at atmospheric pressure also. We made use of a tube of 2 cm. width and of 30 cm. length; the tube being closed at one end and charged with some sal-ammoniac purified by previous sublimation. It is to be recommended to give a preliminary heating to the place where the sal-ammoniac is to be solidified again, in order to decrease the velocity of transition. This procedure also applies to the evacuated tube.

19. Our observations on electric double refraction were continued with the same optical arrangement, described above, but with sal-ammoniac fogs prepared by two methods, differing from the ones used above.

*a.* A current of air was passed successively through bottles with a  $\text{NH}_3$  solution and with a  $\text{HCl}$  solution. The tubes did not reach below the surfaces of the solutions.

The fog, originating in the  $\text{HCl}$  bottle, was introduced into the basin with the exterior condenser plates (see § 10). It was rather difficult to regulate the density, so that the field of view was obscured nearly immediately. The fog was partly precipitated after the interception of the air current and the dark band (§ 3) became visible; the establishment of the field ( $\pm 9000$  volts) made the band jump upwards.

In this case we were unable to observe a downward motion of the band.

In the present experiment the rotation of the plane of polarization (see § 11), i.e. the dichroism was very small, so that it was difficult at first to determine the sign of the rotation. It proved to be, however, the same as the one formerly observed.

In other experiments with the same kind of fog larger rotations were observed.

*b.* Dried air was passed over heated, previously sublimated sal-ammoniac and then introduced into the basin with exterior condenser plates.

The air current and the heating of the sal-ammoniac being well regulated the throwing on of the electric field caused a downward displacement of the band, accompanied with a rotation of the plane of polarization. After stoppage of the air current, the band after a while exhibited the upward displacement. In some experiments the downward displacement could not be observed, and only a rotation was seen. This especially happened, if the density of the fog was initially very great so that the field of view became dark. After partial precipitation of the fog the throwing on of the field caused an upward displacement of the dark band.

20. The results now obtained and those recorded in the former parts of this paper clearly point to the existence of two modifications of sal-ammoniac, the one which is originated first exhibiting a positive, the second modification a negative electric double refraction.

That we may speak of a "direction" of change of the sal-ammoniac modifications is shown by the fact that the positive double refraction is always observed in the first place, and only afterwards the negative refraction; we never observed with a given fog first an upward and then a downward motion of the band.

In some cases the phenomena were only incompletely visible, but this can be always explained.

The downward motion of the band sometimes happened to be absent. This is the case if the air current is very slow. The transition of one modification to the other has already taken place before the introduction of the fog into the condenser.

The upward motion of the band will be imperceptible, if before the entire transition of the fog, the precipitation has been such that the effect becomes too small to be observable.

21. We have tested also a hypothesis, communicated privately to us by a friend, and which would afford a possibility of explaining the observed phenomena, discarding the assumption of two sal-ammoniac modifications.

The orientation of a crystal depends upon the *surrounding medium* and may change with it.

Would it not be possible that in the case of positive double refraction the gas surrounding the particles is different from that present in the case of negative double refraction? For instance hydrochloric acid or ammonia gas in the first case, in the second air with traces only of the mentioned gases. If then the dielectric constant of the environment is not much different from that of the particles, a new orientation might ensue, which would explain the phenomena.

Indeed all the preparations which we used allow of an initial excess of either  $\text{NH}_3$  or  $\text{HCl}$ ; in the experiment with sublimation (§ 19) an excess of one of the constituents might be due to the difference of the velocities of diffusion of the two gases. But in this last experiment air must be abundantly present. In order to look for a possible influence of the surrounding medium, the experiment of § 19 was arranged somewhat differently. A current of air was passed over a solution of  $\text{NH}_3$ , the gases then were dried, and afterwards introduced into the tube, which contained the hot sal-ammoniac and lastly into the space with the condenser plates.

The excess of  $\text{NH}_3$  in the gas delivered from the apparatus was easily shown. The phenomena were the same as those described in § 19*b*).

A similar experiment was tried with  $\text{HCl}$  in excess. The phenomena remained the same. It is preferable to use instead of air passing over a solution of  $\text{HCl}$ , a current of pure hydrochloric acid, obtained by dropping sulphuric acid into hydrochloric acid.

22. We have also established the fact that  $\text{NH}_3$  or  $\text{HCl}$  gas in the

sublimation tube (§ 18) does not prevent the transition of one modification of sal-ammoniac to the other one.

23. From the experiments of §§ 21 and 22 we may conclude, that the observed change of sign of the electric double refraction cannot be explained by a change of orientation of the particles constituting the fog.

24. It seemed interesting to investigate the behaviour of a fog obtained by blowing finely powdered, not very recently sublimated sal-ammoniac into the observation tube, the analogon of the experiment described in § 8 with glass and different tartaric acid salts. The displacement of the dark band ought to be now *upward*. We could confirm this expectation.

25. Recently Prof. VOIGT has been occupied with LANGEVIN's theory. He kindly communicated to us a result, which admits of experimental verification<sup>1)</sup>. From the orientation hypothesis VOIGT deduces, that an absorbing substance must change its power of absorption for *natural* light.

We have sought for an action of this kind using the sal-ammoniac cloud and we think we have discovered it. The nicols and the glass bar of our arrangement were removed. Between the lamp and the lens one or more plates of ground glass were introduced in order to diminish the superfluous intensity of the source of light. A dense sal-ammoniac fog was blown through the observation tube, the field of view becoming of a red hue. Initially the establishing of the field gave no change; after interruption of the air current it caused a brightening of the field of view, later this became darker under the influence of the electric forces.

The first brightening apparently is due to the precipitation of particles on the condenser plates; if the field is made zero again nothing happens. During the later phase very probably an electro-optic effect is observed. The field of view changes from pale yellow, to more red hues. This effect could be observed again and again when the field was put on and off.

26. In the last part of our investigation we will investigate whether

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<sup>1)</sup> Since the above was written VOIGT's paper, Ueber elektrische und magnetische Doppelbrechung. I. was published in Göttinger Nachrichten 1912.

it is possible to determine by the *electro-optic method* a *transition temperature* of the two modifications of the sal-ammoniac fogs, which we have discovered. Other examples will be tried also.

(*To be continued*).

**Chemistry.** — “*On critical end-points in ternary systems. II.* By Prof. A. SMITS. (Communicated by Prof. A. F. HOLLEMAN).

In two previous communications I already discussed some particularities which may occur in ternary systems obtained by the addition to a system of the type ether-anthraquinone of a third substance which presents critical end-points neither with anthraquinone, nor with ether <sup>1)</sup>. An example of this was *naphthaline-ether-anthraquinone*, which was examined by Dr. ADA PRINS <sup>2)</sup>.

Though some more cases were afterwards theoretically examined by me, the publication was postponed not to anticipate too much on the experimental investigation, which was greatly delayed by want of time.

Now however just recently we have met with the very welcome circumstance that the petrographer-mineralogist NIGGLI not only has seen that the phenomena which are found for the said systems, are of fundamental significance for *petrography* and particularly for the *chemistry of the magna*, but that moreover he has had the courage to enter upon an investigation of this territory, which is so comparatively difficult to explore <sup>3)</sup>.

In virtue of this it seemed desirable to publish our results already now, the more so as I may cherish the hope to facilitate the experimental study of others somewhat in this way.

Having discussed one of the possible types pretty fully in my last communication on this subject, a more general discussion of the classification of the different cases which might be distinguished for ternary systems with critical end-points may suffice here.

*1<sup>st</sup> Case.* In the first place I will mention the case that critical end-points occur for only one of the three binary systems; this case was discussed by me before, and tested by an example by Dr. ADA PRINS.

If we call the components *A*, *B*, and *C*, and if critical end-points occur only in the system *A—C*, we know that the ternary system

<sup>1)</sup> These Proc. 25 Sept. 1909. 182.

” ” 24 Sept. 1910. 342.

<sup>2)</sup> These Proc. 24 Sept. 1910. 353.

<sup>3)</sup> Zeitschr. f. Anorg. chem. 75. (1912).



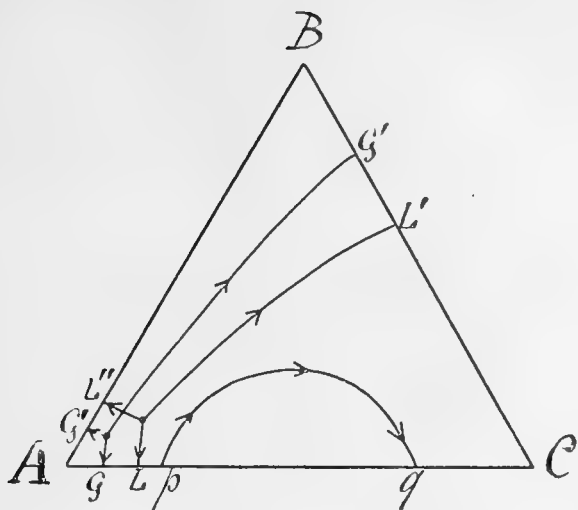


Fig. 1.

see that in the case considered here none of the eutectic lines comes into contact with the critical end-point curve  $pq$ .

*2<sup>nd</sup> Case.* In the second place we shall suppose that in two of the binary systems critical end-points occur, but in such a way that in the symbol for the critical end-point  $S + (G=L)$ , the solid phase  $S$  is the same in the two binary systems. Let the component  $C$  be here this solid phase, then we get the following simple projection on the supposition that the system  $AB$  does not possess either a minimum or a maximum critical temperature.

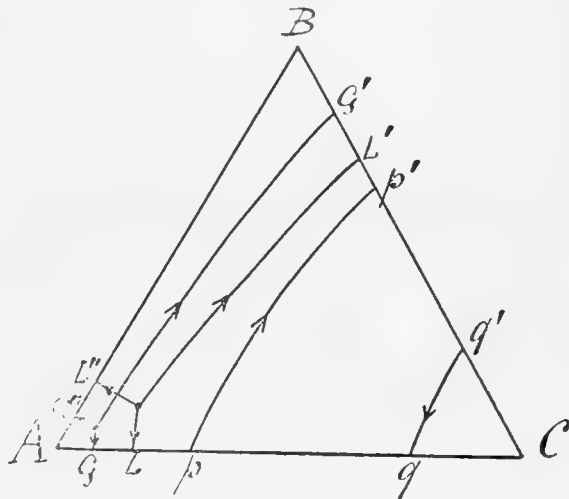


Fig. 2.

Let us consider the case that  $B$  possesses a much higher critical temperature than  $A$ , then the temperature of the critical end-point  $p'$  will probably be higher than that of  $p$ , and hence the temperature will continually rise from  $p$  to  $p'$ . In this case the temperature along the  $q$ -line may rise from  $q'$  to  $q$ , but the reverse is also very well possible; the former has been assumed in the figure. If the system  $AB$  had a minimum critical temperature, the critical end-point lines might get a greater distance, and in the case of a maximum critical temperature depressions can occur which may even give rise to a closed portion, so that a region is formed where no critical end-points occur any more.

*3<sup>rd</sup> case.* The phenomena become much more interesting when the critical end-point curve comes in contact with a eutectic line. This case may be found when in two of the three binary systems critical end-points occur, but so that the solid substance  $S$  in the symbol

will possess a *critical end-point curve*  $pq$ , which projected on the concentration triangle can have a shape as indicated in fig. 1 by the curve  $pq$ , the temperature of which rises in the direction indicated by the arrows.

If in the same triangle we draw the projection of the eutectic vapour and liquid lines, along which the temperature also rises in the direction indicated by the arrows, we

of the critical end-point  $S + (G=L)$  is different in the two binary systems.

So we suppose now that in the two binary systems  $AB$  and  $AC$  critical end-points occur, in such a way that the critical phenomenon appears by the side of solid  $B$  in the system  $AB$ , and by the side of solid  $C$  in the system  $AC$ . A meeting of a eutectic line with a critical end-point curve of course means this that the critical phenomenon occurs at the temperature of the meeting by the side of *two* solid substances, and so it is clear that a eutectic line must always meet *two* critical end-point curves *simultaneously*, namely the critical end-point curves which belong to the solid substances to which the eutectic line refers.

Let us now assume for the sake of simplicity that the melting-point figure of the system  $BC$  possesses a eutectec point. We can then state at once that by the side of the conglomerate of solid  $B +$  solid  $C$  critical phenomena can appear only when the eutectec temperature of the system  $BC$  lies *above* the critical temperature of the component  $A$ , and the greater this difference is the greater will be the chance that the case in question can be realized.

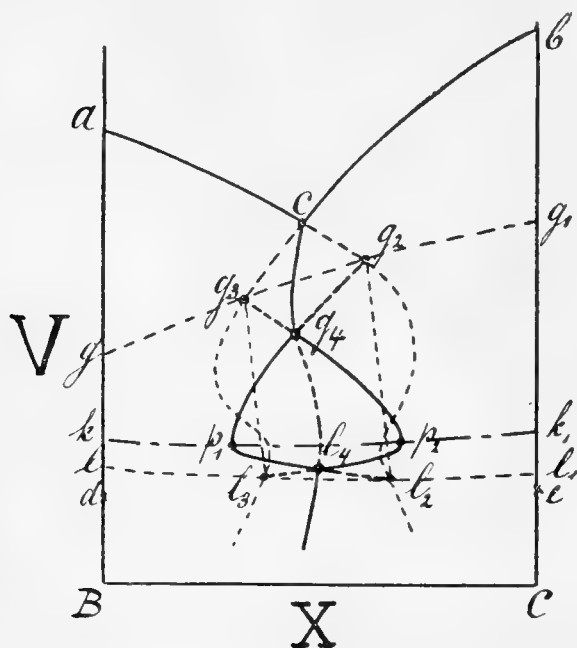


Fig. 3.

vapours, which can coexist with solid  $B$  resp. solid  $C$ .

Now it is of importance to show what equilibria would appear when as we proceed along the isotherm  $ac$  resp.  $bc$  the deposition of solid  $C$  resp. of solid  $B$  did not take place.

This case I examined before in the  $p, x$ -section for another purpose, and the sections discussed then quite agreed with the  $V, X$ -fig. of the system  $B, C$  drawn above<sup>1</sup>).

<sup>1</sup>) These Proc. 30 Dec. 1905. 568.

To get a better insight into the peculiarities of such a system it is necessary to make use of a ternary  $V, X$ -figure, as was used by me before.

This  $V, X$ -figure is pretty simple so that it is possible to give at once the projection of the principal lines of equilibrium on the  $V, X$ -plane of the binary system  $B-C$ .

Below the eutectec temperature the  $V, X$ -figure of the system  $B, C$  consists of two lines  $ac$  and  $bc$ , which indicate the mol. volumes and the concentrations of the

If on compression the deposition of solid  $C$  failed to appear in the vapour coexisting with solid  $B$ , the solubility-isotherm  $acg_2l_2$  shows that in this case a metastable three-phase equilibrium between vapour, liquid, and solid  $B$  might occur, the coexisting phases of which are indicated by the points  $g_2$ ,  $l_2$ , and  $d$ .

The figure also shows that if the vapour that coexists with solid  $C$  could be compressed without solid  $B$  being formed, a metastable three-phase equilibrium between vapour, liquid, and solid  $c$  might appear, indicated by the points  $g_3$ ,  $l_3$ , and  $e$ .

If we now think the third component  $A$  added, and placed in the third angle of the base of the trilateral prism, and if we assume that the chosen temperature lies above that of the first critical end-points in the systems  $AB$  and  $AC$ , it is possible that the stable ternary  $V, X$ -figure simply consists of two isothermal solubility surfaces which intersect along a line which originates in the point  $c$ . Along this ternary solubility isotherm solid  $B + \text{solid } C + \text{vapour}$  coexist. Now it is clear that a two-sheet liquid-vapour surface extends within the said solubility surfaces, which begins on the binodal vapour and liquid line in the plane for  $BC$ . The two sheets of this liquid-vapour-surface will continuously merge into each other in space, and this continuous transition takes place on the critical isotherm, the projection of which on the  $BC$ -plane is indicated by the line  $kk_1$ .

When the said liquid-vapour-surface lies entirely inside the two isothermal solubility surfaces, no critical phenomena can occur in stable condition, and in this case no particularities occur. Now we know that at temperatures lower than those assumed here stable liquid equilibria must occur, and this must also happen when we raise the temperature, and in this way approach the eutectic temperature of the system  $B-C$ . With decrease of temperature we shall see liquid appear as stable phase, because then the liquid-vapour-surface extends more quickly in space than the solubility surfaces. The consequence of this is that at a certain temperature the three-phase solubility isotherm for  $S_B + S_C + G$  just touches the liquid-vapour-surface. So at this moment  $S_B + S_C + L + G$  must be able to coexist for the first time, from which follows that this contact must take place in a point of the critical isotherm of the liquid-vapour surface so that liquid and vapour are identical there, and a critical phenomenon makes its appearance.

In connection with this the following things may be remarked. Starting from the pairs of points  $g_2, l_2$  and  $g_3, l_3$  two continuous curves pass over the liquid-vapour-surface, the former of which indicates the vapours and liquids coexisting with solid  $B$ , and the

latter of which contains the vapours and liquids which can be in equilibrium with solid  $C$ .

If the liquid-vapour-surface touches the solubility isotherm of  $S_B + S_C$ , it is clear that also the lines starting from the nodes  $g_2, l_2$  and  $g_3, l_3$  must touch, which accordingly takes place on the critical isotherm.

If we now think the temperature still a little lower, the just mentioned contact will change into an intersection, and so two points of intersection will occur, one of which indicates the vapour phase, and the other the liquid phase of the four phase equilibrium  $S_B + S_C + L + G$ .

The intersection of these lines, which are indicated in projection by  $g_2, g_4, p_1, l_4, l_2$  and  $g_3, g_4, p_2, l_4, l_3$ , means of course that the liquid-vapour surface intersects the solubility surfaces, in consequence of which the liquid-vapour equilibria get partly into the stable region. These stable liquid-vapour equilibria lie within the two intersecting lines  $g_4, p_1, l_4$  and  $g_4, p_2, l_4$ . The first intersection line, which refers to the liquid and vapour phases which coexist with solid  $B$ , possesses a critical end-point in  $p_1$ , and the second intersection line, which indicates the liquid and vapour phases which can be in equilibrium with solid  $C$ , possesses a critical end-point in  $p_2$ . The points  $g_4$  and  $l_4$  denote, as was already said, the vapour and liquid coexisting with  $S_B + S_C$ , and so it is evident that through these two points the line must pass which has its origin in  $C$ , and indicates the coexistence of a fluid phase with a conglomerate of  $S_B$  and  $S_C$ .

If we lower the temperature still more, the points  $g_4$  and  $l_4$ , and also  $p_1$  and  $p_2$  move more and more apart, whereas on rise of temperature they draw nearer and nearer together, and coincide in the *double critical end-point*, for which the symbol is  $S_B + S_C + (L=G)$ . At temperatures above this *double critical end-point* there will exist only fluid phases or coexistence between fluid phases with solid  $B$  resp. with solid  $C$ , or with the two solid substances at the same time. It is, however, clear that as was already observed, liquid will have to appear again in the ternary system before the eutectic temperature of the system  $B-C$  is reached, and so we see that when at lower temperature a *double critical end-point* has appeared, a second *double critical end-point* will occur at higher temperature, so that then at rise of temperature a repetition will take place of what has happened at lower temperature, but in the reversed order. So after the second double critical end-point has appeared, the stable part of the liquid-vapour-surface will continually increase in extent. To this is added

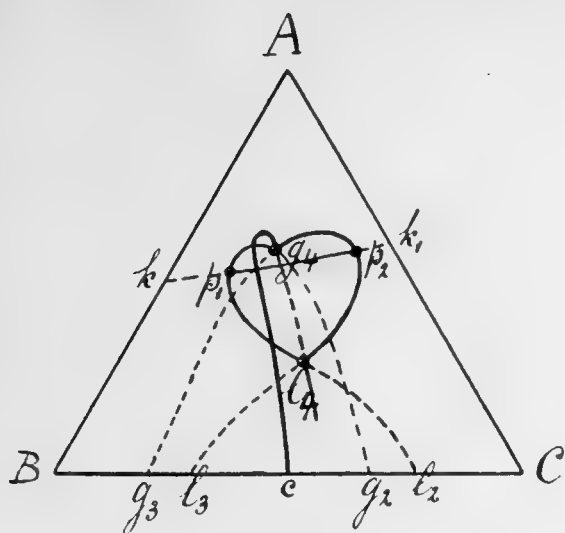


Fig. 4.

lines of the two three-phase equilibria  $S_B + L + G$  and  $S_C + L + G$ , indicated by the letters  $g_3 g_4 p_2 l_3$  resp.  $g_2 g_4 p_1 l_2$  intersect in two points  $g_4$  and  $l_4$ , where four-phase equilibrium prevails, and where accordingly also the fluid line of the three-phase equilibrium  $S_B + S_C + F$  runs, which is denoted by the symbols  $c g_4 l_4$ . It is further noteworthy that the liquid branches of the three-phase equilibria  $S_B + L + G$  and  $S_C + L + G$  are cut by the critical isotherm  $kk_1$ , so that  $p_1$  and  $p_2$  are two critical end-points.

If we start from a temperature lying a little above that of the first critical end-points in the systems  $B-A$  and  $C-A$ , we know that on rise of temperature not only the critical end-points  $p_1$  and  $p_2$ , but also the vapour point  $g_4$  and the liquid point  $l_4$  of the four phase equilibrium  $S_B + S_C + L + G$  will approach each other till they coincide in the *double critical end-point*. As  $g_4$  is a point of the ternary eutectic vapour-line and  $l_4$  a point of the ternary eutectic liquid-line it follows from what precedes that these two ternary eutectic lines will have to pass continuously into each other in the double critical end-point. In the first double critical end-point  $P$  the continuous eutectic line possesses in consequence a *temperature maximum*. At higher temperature the second double critical end-point  $Q$  occurs, and from this temperature the liquid and vapour points of the second continuous part of the eutectic line recede more and more from each other, so that the second double critical end-point is at the same time the *temperature minimum* of the second continuous part of

another particularity in the system  $B-C$  at the temperature of the eutectic point, viz. that the vapour-points  $c g_2 g_3$  and  $g_4$  coincide just as the liquid points  $l_2, l_3$  and  $l_4$ .

Now that this projection has been briefly discussed, it is very easy to project the indicated spacial lines on the concentration triangle, as has been done in fig. 4.

We see from this figure that the two continuous vapour-liquid

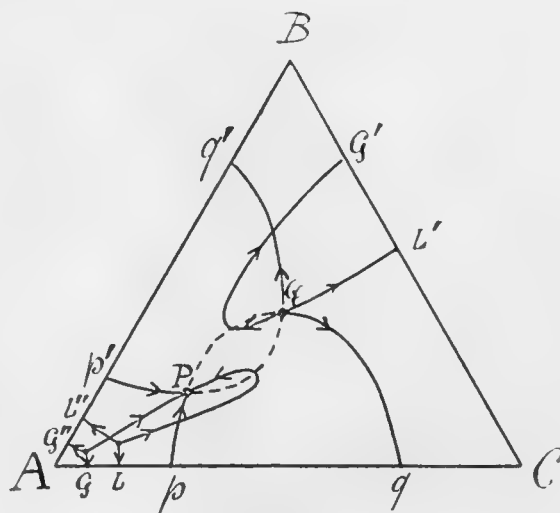


Fig. 5.

the eutectic line. If we represent this in a diagram, i. e. if we draw the projection of the  $p$  $q$ -lines and that of the eutectic lines in the concentration triangle, we get fig. 5, in which the arrows again indicate the direction in which the temperature rises.

It is clear, that it is also possible that the two continuous  $p$  $q$ -lines do not intersect. In this case there are no double critical end-points, and so the eutectic lines proceed undisturbed up to the ternary eutectic point.

*4th case.* In the fourth case we might suppose that each of the binary systems presents critical end-points. To realize this case we shall have to choose three substances, the critical temperatures of which lie apart as far as possible, so that in each binary system the triple point of one component lies far above the critical temperature of the other. If then double critical endpoints occur, we get a combination of fig. 2 and fig. 5.

*5th Case.* It is clear that the appearance of mixed crystals in the system  $B-C$  does not bring about any change in the foregoing considerations, when this system has a eutectic point; if this is not the case, modifications appear which are most considerable when the components  $B$  and  $C$  are miscible in all proportions, as in the system  $\text{SO}_2 + \text{HgBr}_2 - \text{HgJ}_2$ . examined by NIGGLI<sup>1)</sup>. The projection of the critical end-point lines runs then as is schematically represented in fig. 6.

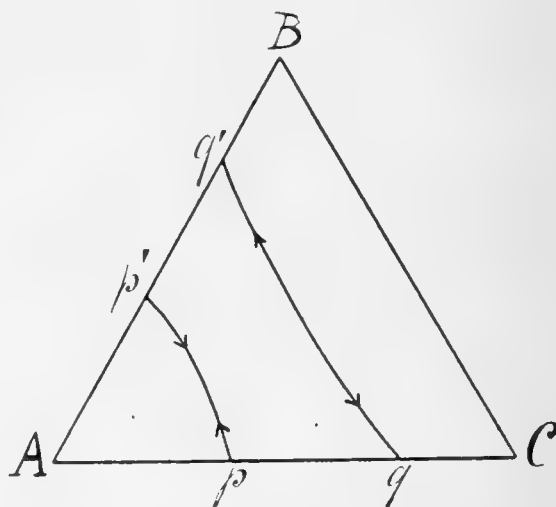


Fig. 6.

Now it should be pointed out, however, that when the melting-point line of the system  $B-C$  has a very marked minimum, a closed portion can be formed in the middle of the figure, so that no critical endpoints occur there then. If on the other hand the said continuous melting-point line has a very marked maximum, the special case might be found that though no critical endpoints occur in the binary systems  $A-B$  and  $A-C$ , they do occur in the ternary system. We can imagine that this case arises from the ordinary case fig. 6 by the points  $p_1$  and  $q_1$ , and also  $p_2$  and  $q_2$  approaching each other and coinciding, in consequence of which the two critical end-point lines merge continuously into one another. If then this continuous curve contracts still further, we have obtained a closed critical end-point curve, which lies quite inside the concentration triangle.

<sup>1)</sup> NIGGLI, The projection.

*6th Case.* If a binary compound appears as a solid phase, different cases may be distinguished, the most interesting of which I will discuss here. In the first place we shall suppose that the components  $B$  and  $C$  do not give critical end-points either with  $A$ , nor with the compound  $BC$ , but that this compound gives critical end-points only with the most volatile component  $A$ . It is clear that when this case occurs, the triple point temperature of the compound  $BC$  will probably lie far above that of the components  $B$  and  $C$ .

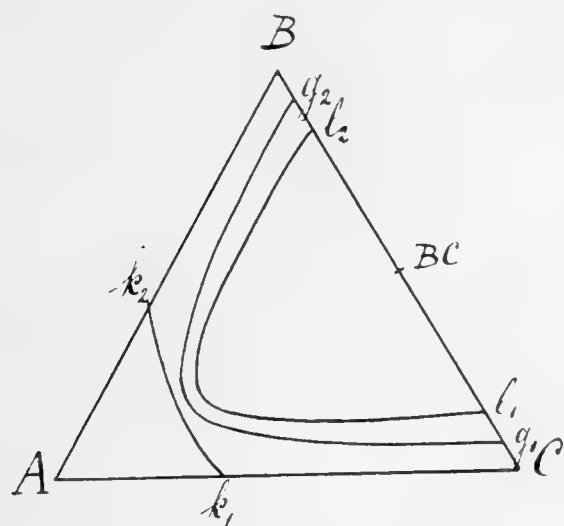


Fig. 7.

seen from  $A$ , as it is supposed here that the compound  $BC$  is less volatile than the components  $B$  and  $C$ . When the liquid vapour surface in the ternary  $v-x$ -figure recedes more on rise of temperature than the surface of nodes for the liquids and vapour coexisting with solid  $BC$ , the critical isotherm will touch this surface of nodes at a given temperature; then the

liquid and the vapour line of this surface of nodes merge continuously into each other. At a still somewhat higher temperature a closed portion is formed in the surface of nodes, in consequence of which two ternary critical end-points have appeared, as fig. 8 shows.

If we think the temperature as gradually rising, the critical end-points will recede from each other in the beginning, and they will also move towards the plane  $BC$ , but before the triple point temperature of the compound has been reached the points  $p_1$  and  $p_2$  will approach each other, and they will coincide, because when we approach the triple point temperature, the surface of nodes of the liquids and vapours that coexist with solid  $BC$  will have to con-

If we draw the projection of the vapour and the liquid line of the three-phase equilibria  $S_{BC} + L + G$  and that of the critical isotherm on the concentration triangle corresponding to a temperature lying above the critical temperature of  $A$  and a little above the highest eutectic temperature of the system  $B-C$ , Fig. 7. is formed.

The isotherm  $k_1k_2$  is convex

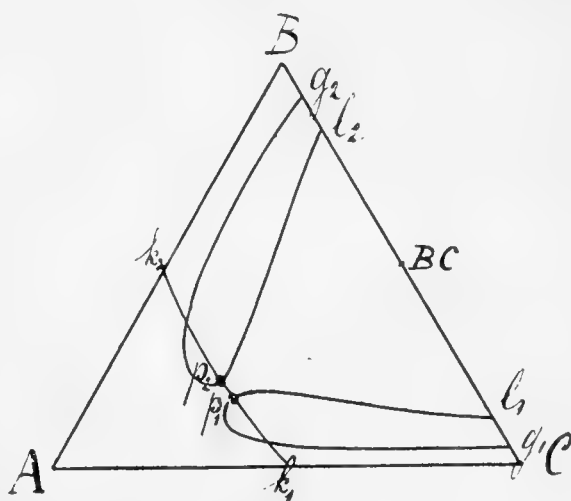


Fig. 8.

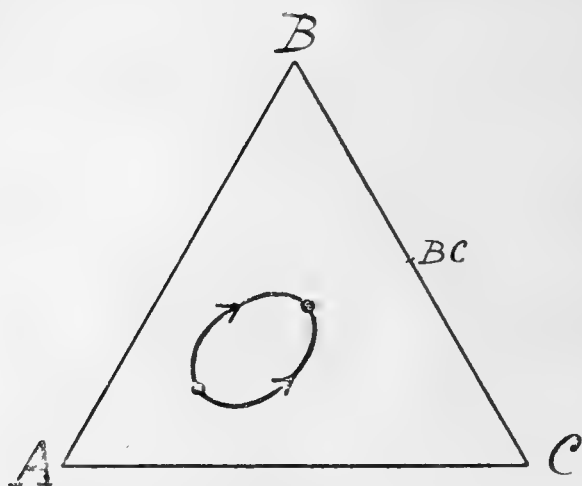


Fig. 9.

tract more rapidly than the liquid-vapour surface, for this surface of nodes entirely disappears at the triple point temperature of  $BC$ . So if we draw the ternary critical end-point line in this case, we get a closed curve, as is drawn in fig. 9 with a temperature minimum and maximum.

If critical end-points occur also in one of the binary systems  $AB$  or  $AC$  or in both, other cases may occur, but they are easy to derive from what precedes. If also ternary compounds are included in our considerations, the cases get somewhat more complicated, as I hope to show on a following occasion.

Amsterdam, June 27 1912.

*Anorg. chemical laboratory  
of the University.*

**Astronomy.** — “*Researches on the orbit of the periodic comet Holmes and on the perturbations of its elliptic motion*”. V. By Dr. H. J. ZWIERS. (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN).

In January 1906 I communicated to this Academy the most probable elements I had derived for the return of the comet Holmes in 1906—07. In a later paper, November 1906, I discussed the then known three photographic observations of the comet by Prof. MAX WOLF at Heidelberg, and from these derived corrections to the mean longitude, to the inclination and to the longitude of the ascending node of the orbit. The elements obtained were:

Epoch 1906 January 16.0 M. T. Greenw.

$$\begin{aligned}
 M_0 &= 351^{\circ}47'36''.838 \\
 \mu &= 517''.447665 \\
 \log a &= 0.5574268 \\
 \varphi &= 24^{\circ}20'25''.55 \\
 i &= 20\ 49\ 0.62 \\
 \tau &= 346\ 2\ 31.63 \\
 \Omega &= 331\ 44\ 37.85
 \end{aligned}
 \left. \vphantom{\begin{aligned} M_0 \\ \mu \\ \log a \\ \varphi \\ i \\ \tau \\ \Omega \end{aligned}} \right\} 1906.0$$

These elements left the following errors O—C in the three observed places:



1906 Aug. 28.55	$\Delta\alpha = + 0^s.095$	$\Delta\delta = - 0".33$
Sept. 25.51	$= + .099$	$= + 1 .26$
Oct. 10.35	$= - .177$	$= - 1 .15$

So the obtained elements very satisfactorily represented the observations, and might therefore be adopted for the apparition in 1906, until by a rigorous calculation of the perturbations this apparition may be exactly combined with the previous ones.

On December 7, however, Prof. WOLF succeeded in taking another observation, this time with the great reflector of 28 inches aperture. It was, however, exceedingly difficult to obtain trustworthy measurements from this last plate. First of all the image of the comet was not sharply defined; "das Bild ist verwaschen, aber deutlich", Prof. WOLF wrote already on Dec. 8. A much greater difficulty arose owing to a peculiarity of the photographic star images, especially on plates taken with reflectors of this shape. The following quotation from a letter of Prof. WOLF of 1906 Dec. 27 may serve to characterize the phenomenon, indicated by him with the name "Verzeichnung".

"Die relative Verzeichnung, ein von mir eingeführtes Wort, ist "der grösste Feind und wichtigste Fehler der fotogr. Positionsbestimmungen. Sie besteht darin, das für jede Sternhelligkeit der zu "messende (Mittel-)punkt des entstehenden Sternscheibchens an anderer "Stelle des Scheibchens zu suchen ist. Also z. B. liegt beim Reflektor "der geometrische Mittelpunkt eines Sternes 9<sup>ter</sup> Grösse in der Nähe "des Gesichtsfeldrandes um mehrere Bogenminuten, soviel ich bis "jetzt schätzen kann, von dem Punkt entfernt, auf den man die "Position eines schwachen Objektes (Cometen) beziehen muss. Für "jede Sterngrösse ändert sich dies, ebenso für jeden Radius ab "optischem Centrum, also  $R = f(r, m)$ . Bei Brashear  $b$  ist die rel. "Verzeichnung erst in  $6^\circ$  radius merkbar. Bei Brashear  $a$  schon in "3°—4°  $r$ . Beim Reflektor schon in 10'—20'  $r$ ."

On the 18<sup>th</sup> of Dec. Prof. WOLF wrote to me:

"Aus A. G. Cambr. 1572 und 1584 erhalte ich für den Kometen  $\alpha_{1906.0} 3^h 38^m 50^s.41 \delta_{1906.0} + 51^\circ 16' 52".7$  1906 Dez. 7  $7^h 8^m.1$  MZ. Kgst.

Grösse 16.

"Ob die relative Verzeichnung ganz richtig eliminiert ist, weiss "ich aber nicht. Ich bringe es auch vorerst nicht heraus. Mir "scheint deshalb, dass das Gewicht dieser Beobachtung etwas "geringer ist, als das der ersten Beobachtungen."

With the scarcity of the material this observation too demanded the necessary attention but after what has been said above I need

hardly mention that I commenced the calculations for it with little hope of success.

For the reduction to apparent place I found:

$$\text{in } \alpha : +5^s.112 \qquad \text{in } \delta : +9''.75$$

and as correction for parallax:

$$\text{in } \alpha : -0^s.247 \qquad \text{in } \delta : +0''.72$$

The observed apparent place thus becomes:

$$1906 \text{ Dec. } 7.273046 : \alpha = 3^h 38^m 55^s.275 \quad \delta = +51^\circ 17' 3''.17$$

$$\text{Time of aberration: } 0.011279 \text{ day.}$$

This observation has further been treated in exactly the same way as the three preceding ones in my communication of Nov. 1906. As starting-elements I again adopted those given in my paper of January 1906, p. 677, after increasing  $M$  with  $50''$ . I obtained as differences Obs.—Comp.:

$$1906 \text{ Dec. } 7.27 : \Delta \alpha = +1^s.065 \quad \Delta \delta = +15''.53$$

For the derivation of the differential quotients of  $\alpha$  and  $\delta$  with respect to  $M$ ,  $i$  and  $\Omega$  the computed places were then derived 1. with  $\Delta M = +40''$  (instead of  $+50''$ ); 2. with  $\Delta i = +10''$ ; 3. with  $\Delta \Omega = +10''$ . Thus this fourth place yielded the two following equations of condition:

$$\text{From } \alpha : +0.2288 \Delta M - 0.0372 \Delta i - 0.0114 \Delta \Omega = +1^s.065$$

$$\text{From } \delta : +0.426 \Delta M + 1.374 \Delta i + 0.033 \Delta \Omega = +15''.53.$$

The first equation was again multiplied by  $15 \cos \delta$  and just as before  $\frac{\Delta \Omega}{10}$  was introduced as unknown quantity instead of  $\Delta \Omega$ ; moreover I gave half weight to both equations. Thus I obtained 2 new equations, in addition to the former six, given in my paper Researches IV (Nov. 1906):  
from the R. A.:

$$0.18128 \Delta M + 9.39236_n \Delta i + 9.87872_n \frac{\Delta \Omega}{10} = 0.84917$$

from the declination:

$$9.47889 \Delta M + 9.98747 \Delta i + 9.36799 \frac{\Delta \Omega}{10} = 1.04067$$

in which all co-efficients are logarithmic.

From the total of 8 equations of condition there follow the normal equations:

$$\begin{aligned}
 + 12.3229 \Delta M - 0.47796 \Delta i - 4.9039 \frac{\Delta \Omega}{10} &= - 17.461 \\
 - 0.47796 \text{ ,, } + 5.1423 \text{ ,, } - 2.3300 \text{ ,, } &= + 58.562 \\
 - 4.9039 \text{ ,, } - 2.3300 \text{ ,, } + 4.4680 \text{ ,, } &= - 26.733.
 \end{aligned}$$

These give the following values for the corrections of the elements:

$$\begin{aligned}
 \Delta M &= - 2''.6793 \\
 \Delta i &= + 9.29 \\
 \Delta \Omega &= - 40.78
 \end{aligned}$$

By means of substitution in the equations of condition we find that these corrections leave the following errors O—C in the observations :

1906 Aug. 28.55	$\Delta \alpha = - 0^s.190$	$\Delta \delta = - 0''.11$
Sept. 25.51	$- 0.207$	$+ 0.72$
Oct. 10.35	$- 0.510$	$- 2.26$
Dec. 7.27	$+ 1.559$	$+ 5.25$

The now found corrections of the elements do not differ considerably from those determined before, but a comparison of the remaining errors shows that the introduction of the uncertain fourth place in the calculation cannot be said to have improved matters. Therefore I continue to regard the elements given at the beginning of this paper and agreeing absolutely with those from the "Proceedings" of Nov. 1906, as the most accurate for the present moment.

For the approaching return of the comet I have kept these elements unaltered since there was no time to calculate the perturbations. I have only reduced the elements  $i$ ,  $\pi$  and  $\Omega$  to the ecliptic and the aequinox of 1912.0. So the employed elements are :

$$\begin{aligned}
 &\text{Epoch 1912 June 15.0 M. T. Greenw.} \\
 &M = 328^\circ 25' 19''.269 \\
 &\mu = 517''.447665 \\
 &T = 1913 \text{ January } 20.695 \text{ M. T. Gr.} \\
 &\log a = 0.557427 \\
 &\varphi = 24^\circ 20' 25''.6 \\
 &\left. \begin{aligned} i &= 20 \ 49 \ 3 \ .3 \\ \pi &= 346 \ 7 \ 32 \ .9 \\ \Omega &= 331 \ 49 \ 42 \ .1 \end{aligned} \right\} 1912.0
 \end{aligned}$$

According to these elements circumstances are not quite so favourable this time. The perihelion passage occurs shortly before the con-

junction with the sun so that the comet is then at a great distance from the earth and its place in the heavens is moreover not far from the sun. The circumstances are more favourable at the opposition in 1912, although the comet then remains invisible for our northern regions owing to its considerable southern declination. In order to calculate an ephemeris for that opposition I have first derived the following expressions for the heliocentric co ordinates :

$$\begin{aligned}x &= [9.99\ 3799] \sin (v + 77^{\circ}42'18''.3) \\y &= [9.87\ 6101] \sin (v - 20\ 52\ 48.5) \\z &= [9.83\ 2770] \sin (v - 1\ 43\ 55.6)\end{aligned}$$

The rectangular solar co-ordinates have been taken from the Nautical Almanac and reduced to the mean aequinox of the beginning of the year.

The resulting mean places of the comet were reduced to the aequinox of the date by means of the constants  $f$ ,  $g$ ,  $G$  of the Naut. Alm.

The following table gives the apparent places of the comet for Greenwich mean noon; column  $H$  gives the theoretical brightness according to  $H = \frac{1}{r^2 q^2}$ . It may be remembered, that the value of  $H$  for the time of the photographs by WOLF in 1906 varied between 0.032 and 0.038.

Apparent places of the comet from 1912 June 15 to 1913 Jan. 1  
for 0<sup>h</sup> mean time at Greenwich.

1912	$\alpha$	$\delta$	$\log \rho$	$H$
	h m s	° ' "		
June 15	19 23 29.74	— 49 16 38.2	0.24 0106	0.0473
17	21 41.65	20 43.5	0.23 6066	
19	19 46.28	23 59.7	2204	.0497
21	17 44.08	26 21.6	0.22 8530	
23	15 35.55	27 43.9	5051	.0519
25	13 21.29	28 3.2	1779	
27	11 1.95	27 16.6	0.21 8719	.0541
29	8 38.22	25 21.3	5878	
July 1	6 10.91	22 14.7	3263	.0561
3	3 40.82	17 54.9	0878	
5	1 8.82	12 19.3	0.20 8732	.0580
7	18 58 35.69	5 26.4	6828	
9	56 2.35	— 48 57 15.7	5172	.0596
11	53 29.71	47 47.7	3764	
13	50 58.71	37 2.5	2608	.0611
15	48 30.30	25 0.2	1706	
17	46 5.39	11 42.4	1058	.0622
19	43 44.82	— 47 57 11.1	0660	
21	41 29.38	41 30.6	0510	.0631
23	39 19.87	24 42.5	0603	
25	37 16.84	6 50.5	0935	.0637
27	35 20.86	— 46 47 58.3	1504	
29	33 32.44	28 9.8	2302	.0640
31	31 52.05	7 29.1	3322	
Aug. 2	30 20.08	— 45 46 0.3	4558	.0641
4	28 56.87	23 47.6	6004	
6	27 42.67	0 55.1	7651	.0639
8	26 37.69	— 44 37 26.8	9492	
10	25 42.13	13 26.9	0.21 1522	.0635
12	24 56.14	— 43 48 59.5	3728	
14	24 19.80	24 8.9	6103	.0629
16	23 53.11	— 42 58 58.7	8634	
18	23 36.05	33 32.6	0.22 1309	.0620
20	23 28.54	7 53.4	4124	
22	23 30.42	— 41 42 4.6	7065	.0611
24	23 41.53	16 8.9	0.23 0124	
26	24 1.68	— 40 50 8.9	3291	.0600
28	24 30.72	24 6.4	6559	
30	25 8.35	— 39 58 3.5	9918	.0588
Sept. 1	25 54.37	32 1.8	0.24 3360	
3	26 48.58	6 2.7	6879	.0576
5	27 50.86	— 38 40 7.0	0.25 0470	
7	29 0.94	14 16.3	4121	.0563
9	30 18.57	— 37 48 31.3	7825	
11	31 43.54	22 52.8	0.26 1575	.0549
13	33 15.68	— 36 57 21.1	5370	
15	34 54.72	31 56.2	9197	.0536
17	36 40.39	6 38.2	0.27 3049	
19	38 32.44	— 35 41 27.3	6921	.0522
21	40 30.62	16 23.7	0.28 0810	
23	42 34.68	— 34 51 27.2	4709	.0509
25	44 44.37	26 37.3	8613	
27	46 59.46	1 53.7	0.29 2518	.0496
29	49 19.72	— 33 37 15.3	6423	

1912/13	$\alpha$	$\delta$	$\log \rho$	$H$
	h m s	° ' "		
Oct. 1	18 51 44.96	— 33 12 41.9	0.30 0324	0.0483
3	54 14.99	— 32 48 12.8	4217	
5	56 49.62	23 47.3	8098	.0470
7	59 28.72	— 31 59 24.6	0.31 1966	
9	19 2 12.10	35 4.0	5817	.0458
11	4 59.57	10 45.0	9648	
13	7 50.95	— 30 46 26.7	0.32 3455	.0446
15	10 46.07	22 8.6	7235	
17	13 44.73	— 29 57 49.5	0.33 0986	.0434
19	16 46.75	33 28.8	4707	
21	19 51.95	9 5.6	8397	.0423
23	23 0.18	— 28 44 40.0	0.34 2052	
25	26 11.28	20 10.3	5672	.0412
27	29 25.12	— 27 55 36.0	9257	
29	32 41.57	30 56.3	0.35 2807	.0402
31	36 0.47	6 10.7	6320	
Nov. 2	39 21.75	— 26 41 18.4	9795	.0392
4	42 45.30	16 18.9	0.36 3231	
6	46 11.01	— 25 51 11.4	6626	.0383
8	49 38.74	25 55.3	9981	
10	53 8.41	0 30.1	0.37 3294	.0374
12	56 39.92	— 24 34 55.3	6564	
14	20 0 13.14	9 10.4	9789	.0365
16	3 47.93	— 23 43 14.4	0.38 2970	
18	7 24.20	17 7.6	6107	.0357
20	11 1.85	— 22 50 49.6	9198	
22	14 40.78	24 20.0	0.39 2245	.0349
24	18 20.90	— 21 57 38.1	5248	
26	22 2.13	30 43.8	8206	.0342
28	25 44.40	3 36.9	0.40 1120	
30	29 27.67	— 20 36 17.1	3990	.0334
Dec. 2	33 11.89	8 44.1	6817	
4	36 56.98	— 19 40 57.7	9600	.0327
6	40 42.88	12 57.6	0.41 2337	
8	44 29.53	— 18 44 43.6	5029	.0321
10	48 16.89	16 15.6	7677	
12	52 4.87	— 17 47 33.6	0.42 0278	.0314
14	55 53.40	18 37.7	2833	
16	59 42.42	— 16 49 27.9	5342	.0308
18	21 3 31.90	20 4.2	7808	
20	7 21.77	— 15 50 26.8	0.43 0229	.0302
22	11 11.94	20 35.7	2605	
24	15 2.38	— 14 50 30.9	4937	.0297
26	18 53.14	20 12.6	7227	
28	22 44.16	— 13 49 41.0	9474	.0291
30	26 35.41	18 56.1	0.44 1679	
Jan. 1	30 26.86	— 12 47 58.2	3842	.0286

The following table gives the variations of  $\alpha$  and  $\delta$  in two suppositions: 1st that the comet reaches its perihelion 4 days earlier, 2nd that it reaches it 4 days later.

Variations of  $\alpha$  and  $\delta$  for altered times of perihelion passage.

1912/13	$\Delta T = -4d$		$\Delta T = +4d$	
	$\Delta\alpha$	$\Delta\delta$	$\Delta\alpha$	$\Delta\delta$
	m s	' "	m s	' "
June 15	+ 8 43.27	+ 33 58.7	- 8 46.83	- 31 17.0
19	+ 8 56.85	+ 33 20.7	- 8 59.63	- 30 29.0
23	+ 9 8.79	+ 32 27.1	- 9 10.67	- 29 28.8
27	+ 9 18.52	+ 31 21.2	- 9 19.43	- 28 15.7
July 1	+ 9 26.01	+ 30 5.4	- 9 25.48	- 26 55.1
5	+ 9 30.67	+ 28 44.1	- 9 28.94	- 25 28.0
9	+ 9 32.35	+ 27 15.7	- 9 29.29	- 24 1.4
13	+ 9 31.05	+ 25 48.7	- 9 26.57	- 22 34.2
17	+ 9 26.66	+ 24 25.8	- 9 21.08	- 21 13.8
21	+ 9 19.67	+ 23 9.2	- 9 12.89	- 20 1.7
25	+ 9 10.05	+ 22 3.5	- 9 2.62	- 19 0.5
29	+ 8 58.51	+ 21 10.2	- 8 50.35	- 18 13.6
Aug. 2	+ 8 45.41	+ 20 30.5	- 8 36.79	- 17 40.0
6	+ 8 31.09	+ 20 5.8	- 8 22.31	- 17 21.8
10	+ 8 16.05	+ 19 54.1	- 8 7.19	- 17 17.0
14	+ 8 0.57	+ 19 55.7	- 7 51.87	- 17 25.5
18	+ 7 45.05	+ 20 9.8	- 7 36.55	- 17 45.1
22	+ 7 29.69	+ 20 34.6	- 7 21.55	- 18 15.8
26	+ 7 14.73	+ 21 8.7	- 7 6.95	- 18 54.5
30	+ 7 0.13	+ 21 50.0	- 6 52.95	- 19 40.4
Sept. 3	+ 6 46.33	+ 22 37.9	- 6 39.42	- 20 31.9
7	+ 6 32.95	+ 23 29.3	- 6 26.75	- 21 28.1
11	+ 6 20.36	+ 24 24.7	- 6 14.53	- 22 27.1
15	+ 6 8.45	+ 25 23.3	- 6 3.09	- 23 27.8
19	+ 5 57.10	+ 26 21.3	- 5 52.24	- 24 30.5
23	+ 5 46.43	+ 27 20.7	- 5 42.05	- 25 33.3
27	+ 5 36.33	+ 28 21.2	- 5 32.41	- 26 35.1
Oct. 1	+ 5 26.80	+ 29 20.5	- 5 23.28	- 27 36.7
5	+ 5 17.87	+ 30 18.3	- 5 14.67	- 28 37.4
9	+ 5 9.37	+ 31 14.5	- 5 6.56	- 29 37.7
13	+ 5 1.33	+ 32 9.7	- 4 58.86	- 30 35.4
17	+ 4 53.74	+ 33 3.7	- 4 51.57	- 31 31.8
21	+ 4 46.53	+ 33 54.6	- 4 44.61	- 32 25.4
25	+ 4 39.73	+ 34 45.2	- 4 38.02	- 33 18.5
29	+ 4 33.21	+ 35 32.7	- 4 31.80	- 34 9.4
Nov. 2	+ 4 27.07	+ 36 17.9	- 4 25.81	- 34 58.1
6	+ 4 21.13	+ 37 1.6	- 4 20.18	- 35 44.3
10	+ 4 15.58	+ 37 42.5	- 4 14.69	- 36 28.7
14	+ 4 10.28	+ 38 24.1	- 4 9.55	- 37 10.5
18	+ 4 5.19	+ 38 58.8	- 4 4.61	- 37 50.8
22	+ 4 0.37	+ 39 33.7	- 3 59.89	- 38 28.0
26	+ 3 55.77	+ 40 5.8	- 3 55.44	- 39 3.8
30	+ 3 51.43	+ 40 36.0	- 3 51.11	- 39 37.0
Dec. 4	+ 3 47.25	+ 41 3.8	- 3 47.07	- 40 8.1
8	+ 3 43.33	+ 41 29.8	- 3 43.15	- 40 36.5
12	+ 3 39.59	+ 41 52.9	- 3 39.51	- 41 3.4
16	+ 3 36.07	+ 42 14.4	- 3 35.99	- 41 27.4
20	+ 3 32.65	+ 42 33.4	- 3 32.75	- 41 49.5
24	+ 3 29.60	+ 42 50.2	- 3 29.54	- 42 9.4
28	+ 3 26.63	+ 43 4.5	- 3 26.64	- 42 27.0
Jan. 1	+ 3 23.84	+ 43 16.8	- 3 23.88	- 42 41.8

Leyden, June 1912.

**Mathematics.** — “*The scale of regularity of polytopes*”. By Dr. E. L. ELTE (Meppel). (Communicated by Prof. P. H. SCHOUTE).

In my dissertation<sup>1)</sup> it was my aim to determine the semiregular polytopes, i. e. the polytopes analogous to the semiregular polyhedra. So this investigation had to be based on a definition of the notion “semiregular polytope”. Now ordinarily a semiregular polyhedron is defined as follows: “A semiregular polyhedron has *either* congruent (or symmetric) vertices and regular faces *or* congruent faces and regular vertices. So there are two kinds of semiregular polyhedra which we will call with CATALAN<sup>2)</sup> “semiregular of the first kind” and “semiregular of the second kind”; those of the first kind are enumerated in the following table. For any of these polyhedra this table gives the numbers of vertices, edges, faces and indicates which faces pass through each vertex and which couples of faces pass through each kind of edges. Here  $p_n$  denotes a regular polygon with  $n$  vertices.

Notation	N <sup>o</sup>	Vertices	Edges	Faces	Faces through a vertex	Faces through the edges		
tT	1	12	18	8	$1p_3, 2p_6$	$p_6, p_6$	$p_6, p_3$	
tC	2	24	36	14	$1p_3, 2p_8$	$p_8, p_8$	$p_8, p_3$	
tO	3	24	36	14	$1p_4, 2p_6$	$p_6, p_6$	$p_6, p_4$	
tD	4	60	90	32	$1p_3, 2p_{10}$	$p_{10}, p_{10}$	$p_{10}, p_3$	
tI	5	60	90	32	$1p_5, 2p_6$	$p_6, p_6$	$p_6, p_5$	
CO	6	12	24	14	$2p_3, 2p_4$	$p_4, p_3$		
ID	7	30	60	32	$2p_3, 2p_5$	$p_5, p_3$		
RCO	8	24	48	26	$1p_3, 3p_4$	$p_4, p_4$	$p_4, p_3$	
RID	9	60	120	62	$1p_3, 2p_4, 1p_5$	$p_4, p_5$	$p_4, p_3$	
tCO	10	48	72	26	$1p_4, 1p_6, 1p_8$	$p_6, p_8$	$p_4, p_8$	$p_4, p_6$
tID	11	120	180	62	$1p_4, 1p_6, 1p_{10}$	$p_{10}, p_6$	$p_{10}, p_4$	$p_4, p_6$
CS	12	24	60	38	$1p_4, 4p_3$	$p_4, p_4$	$p_3, p_3$	
DS	13	60	150	92	$1p_5, 4p_3$	$p_5, p_3$	$p_3, p_3$	
$P_n$	14	$2n$	$3n$	$n + 2$	$1p_n, 2p_4$	$p_n, p_4$	$p_4, p_4$	
$AP_n$	15	$2n$	$4n$	$2n + 2$	$1p_n, 3p_3$	$p_n, p_3$	$p_3, p_3$	

1) “The semiregular polytopes of the hyperspaces”, Groningen, 1912.

2) “Mémoire sur la théorie des polyèdres”, *Journal de l'École Polytechnique*, Cahier 47.



The semiregular polytopes of the second kind are the polar-reciprocal figures of those given in the table with respect to a concentric sphere.

The definition of semiregular polyhedron given above had to be modified in order to make it applicable to polydimensional spaces.

We say that a polyhedron possesses a "characteristic of regularity", if either all the vertices, or all the edges, or all the faces are equal to each other. Equality of vertices signifies that the polyangles formed by the edges concurring in each vertex are congruent (or symmetric); equality of faces consists in the congruency of the limiting polygons. But the equality of edges includes two different parts which can present themselves each for itself: equality in length of the edges and equality of the angles of position of the faces through the edges. So all the polyhedra of the table have edges of the same length but -- with exception of the numbers 6 and 7 -- more than one kind of angles of position, whilst quite the reverse presents itself with the corresponding polyhedra of the second kind. If the equality of edges is realized only partially -- as in the case of the polyhedra of the table -- we speak of a "half characteristic" so that these polyhedra admit  $1\frac{1}{2}$  characteristics. By bringing this result in connection with the circumstance that a polyhedron can admit 3 characteristics, the epitheton "semiregular" obtains a *literary* signification. As the polyhedra N<sup>o</sup>. 6 and N<sup>o</sup>. 7 of the table possess both the half characteristics of the edges, these polyhedra must be called " $\frac{2}{3}$ -regular" according to our system.

We remark that the characteristics of a semiregular polyhedron of one of the two kinds are lacking in the corresponding polyhedron of the other. Moreover that we are obliged to observe a quite determinate order of succession in counting the characteristics of a polyhedron of defined kind and, beginning at the commencement, to count successive characteristics only, i. e. in the case of polyhedra of the first kind to take into account successively equality of vertices, equality in length of edges, equality of angles of position round edges, equality of faces, and reversely in the case of polyhedra of the second kind. If this order of succession was not observed e. g. with respect to the two half characteristics of the edges a beam with different length, breadth, and height would appear as a semiregular polyhedron of the first kind on account of equality of vertices and angles of position, whilst a double pyramid formed by the superposition of two faces of two equal regular tetrahedra would appear as a semiregular polyhedron of the second kind, to which enunciations fundamental objections can be raised.

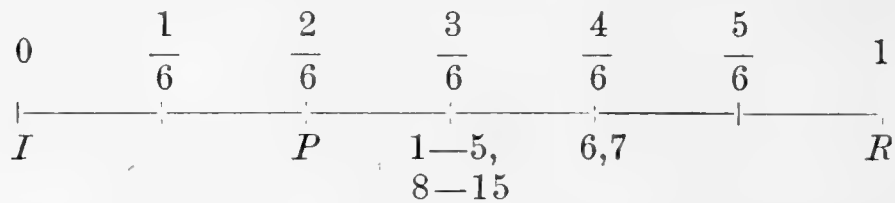
Now the *definition* of “degree of regularity” extended to higher spaces runs as follows:

“The degree of regularity of an  $n$ -dimensional polytope is a fraction with  $n$  as numerator and the number  $p$  of the successive characteristics of regularity as denominator, this number  $p$  being counted in the case of a polytope of the first kind from the vertex end, in the case of a polytope of the second kind from the end of the limiting  $n-1$ -dimensional polytope.”

In my dissertation I have confined myself to polytopes of the first kind, the degree of regularity of which is  $\frac{1}{2}$  at least. For the methods employed in unearthing these polytopes I must refer to that memoir.

In discussing my dissertation my promotor Dr. P. H. SCHOUTE remarked that if all the fractions representing possible degrees of regularity of an  $n$ -dimensional polytope are reduced to the denominator  $2n$  the numerators 1 and  $2n-1$  will be lacking, on account of the fact that the first and the last characteristic have not been subdivided into two halves; so in this sense my scale contains something superfluous.

Indeed the classification of the polyhedra according to my scale is indicated in the diagram

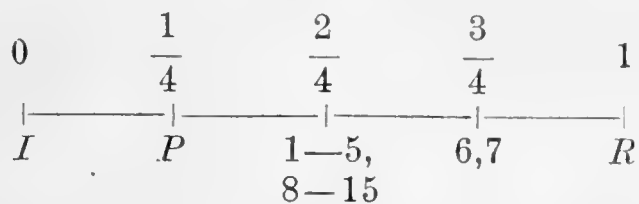


where the numbers 1—5, 8—15 at the midpoint and 6,7 at the right designate the polyhedra bearing these numbers in the table, whilst  $I$  and  $R$  stand for quite irregular and regular polyhedra and  $P$  either for the beam or for the double pyramid mentioned above, according to the scale corresponding either to polyhedra of the first or to polyhedra of the second kind. Indeed the points of division  $\frac{1}{6}$  and  $\frac{5}{6}$  are unoccupied and in  $S_n$  the analogous characteristic

property presents itself with respect to the points of division  $\frac{1}{2n}$  and  $\frac{2n-1}{2n}$ .

It goes without saying that we can take away the superfluity indicated (of the two points of division adjacent on either side to the extremities) *either* by counting each of the two extreme charact-

eristics, that of the vertices and that of the limiting  $n-1$ -dimensional polytopes, for half a characteristic, *or* — what comes to the same — by counting each of the two extreme characteristics and each of the two halves of the remaining intermediate characteristics for one. So the scale relating to our space passes into



where the numbers and the letters have the same meaning as above. An  $n$ -dimensional polytope of the degree of regularity  $\frac{p}{n}$  according to the scale given in my dissertation will be qualified, for  $1 \leq p \leq n-1$ , by the degree of regularity  $\frac{p-\frac{1}{2}}{n-1}$  according to the new scale, whilst this degree would acquire the same value for both scales in the cases  $p=0$  and  $p=n$ , i.e. for entirely irregular and for regular polytopes. For in the cases  $1 \leq p \leq n-1$  a polytope loses in the first of the two possibilities indicated by *either* and *or* a half characteristic, whilst the total number of available characteristics diminishes by a half at either side which changes the denominator  $n$  into  $n-1$ .

In this paper I wish to take position with respect to the modification of my scale due to Dr. SCHOUTE. Thereby I will have occasion to point out three different moments.

1. Besides for entirely irregular and for regular polytopes the two scales coincide with respect to semiregular polytopes proper. For the supposition

$$\frac{p}{n} = \frac{p-\frac{1}{2}}{n-1}$$

gives

$$2p(n-1) = n(2p-1),$$

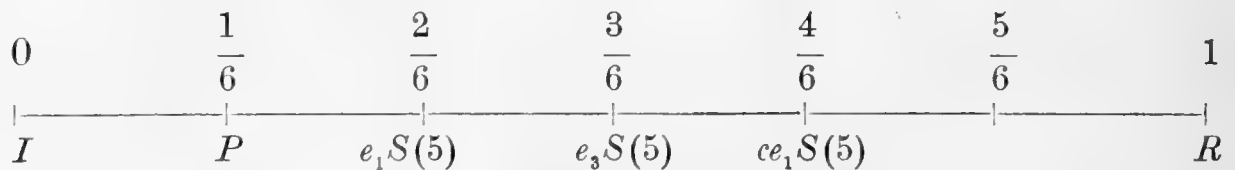
i. e.  $p = \frac{1}{2}n$  and therefore

$$\frac{p}{n} = \frac{p-\frac{1}{2}}{n-1} = \frac{1}{2}.$$

So, if we arrange the polytopes of space  $S_n$  in three groups, for which the degree of regularity is successively smaller than a half, equal to a half and larger than a half the modification proposed brings no alteration in these groups. Otherwise: in passing to the new scale the polytopes with a degree of regularity equal to a half

do not stir, whilst — if we use scales of the same length — the others execute a movement enlarging their distance from the centre. So the polytopes with a degree of regularity of at least a half found by me present themselves quite as well if we use the new scale; so in this respect I have not the least objection to accept this new scale. <sup>1)</sup>

2. However one may not flatter oneself with the hope, that the new scale shall not contain superfluous points of division with respect to either of the two kinds of polytopes considered for itself. In space  $S_4$  already we find with respect to the polytopes of the first kind in this new scale, agreeing with the old one for  $n = 3$ , the point of division  $\frac{5}{6}$  unoccupied. For we have



where  $I$  and  $R$  have the same meaning as before, whilst  $P$  represents a rectangular parallelotope with edges of four different lengths and  $e_1S(5)$ ,  $e_3S(5)$ ,  $ce_1S(5)$  indicate three polytopes deduced from the regular simplex  $S(5)$  of  $S_4$  in the notation given by Mrs. A. BOOLE STOTT <sup>2)</sup>.

3. As the new scale contains no unoccupied points of division in the case  $n = 3$  only, it would not be worth while to substitute it for mine, which has the advantage of treating all the groups of limiting elements — vertices, edges, faces, etc. and the limits with the highest number of dimensions — on the same footing, if it did not possess a second advantage, in my opinion of great importance. We will treat this somewhat in detail.

In the determination of the semiregular polytopes of the first kind I consider of any polytope the corresponding “vertex polytope” <sup>3)</sup>. In general the vertices of the latter are those vertices of the former joined by edges to a vertex of this original polytope. In an appendix to my dissertation I state the rule, that a polytope with edges of

<sup>1)</sup> Dr. SCHOUTE requests me to communicate that the primitive idea of this new scale for  $S_n$  presented itself to him in an intercourse with F. ZERNIKE, candidate in mathematics and physics at the University of Amsterdam.

<sup>2)</sup> “Geometrical deduction of semiregular from regular polytopes and space fillings”, *Verh. Kon. Akad. v. Wetenschappen*, Amsterdam, 1st series, Vol. XI, n<sup>o</sup>. 1.

<sup>3)</sup> Not to be confounded with the polytope of vertex import of Mrs. A. BOOLE STOTT.

the same length <sup>1)</sup> admits one characteristic of regularity more than its vertex polytope, i.e. if the latter is  $n$ -dimensional and admits the degree of regularity  $\frac{p}{n}$ , the former must admit the degree of regularity

$\frac{p+1}{n+1}$ . In this rule the indicated modification of the scale evidently does not bring any alteration. If we build up an  $n+1$ -dimensional polytope by starting from a given  $n$ -dimensional vertex polytope, the  $n+1$ -dimensional polytope will possess all the characteristics of regularity of the  $n$ -dimensional one, each of these adapted to limiting elements of one dimension higher, and moreover it obtains at the beginning of the series two new halves of characteristics, i.e. equal vertices and edges of the same length. Finally the denominator likewise increases by unity, the new polytope admitting one dimension more than its vertex polytope.

In my dissertation I had to point out an exception to this rule, presenting itself in the case  $p=0$ , i.e. when the vertex polytope is irregular. For in that case  $\frac{0}{n}$  passes into  $\frac{1\frac{1}{2}}{n+1}$  instead of  $\frac{1}{n+1}$ . So the vertex polytope of the semiregular polyhedra of the table — i.e. “the vertex polygon” here — is an isosceles triangle for the numbers 1—5 and 14, an isosceles trapezium for 8, 9, 15, a scalene triangle for 10, 11, a symmetric pentagon for 12, 13 and therefore the degree of regularity  $\frac{0}{2}$  of the vertex polygon has to lead to  $\frac{1\frac{1}{2}}{3} = \frac{1}{2}$  in the cases enumerated. This exception now disappears by introduction of the new scale of Dr. SCHOUTE; for according to this scale  $\frac{0}{1}$  passes into  $\frac{1}{2}$  in these cases.

On account of the latter important advantage of the new scale over the old one I wish to accept the first. Therefore I insert finally a second table in which the polydimensional polytopes with a degree of regularity equal to or surpassing  $\frac{1}{2}$  are enumerated with addition of their degree of regularity according to the new scale.

The superscripts  $S_n$  represent the number of the  $n$ -dimensional limits of the polytope. The character of these limits is indicated by notations, the meaning of which is partially clear by itself or by the first table of this paper. Moreover we may state the meaning of the following symbols:

<sup>1)</sup> The latter has been supposed tacitly on p. 129.

Degree	Notation	$S_0$	$S_1$	$S_2$	$S_3$	$S_4$	$S_5$	$S_6$	$S_7$
4:6	$tC_5$	10	30	$(10 + 20)p_3$	$5O + 5T$				
3:6	$tC_8$	32	96	$64p_3 + 24p_4$	$8CO + 16T$				
3:6	$tC_{24}$	96	288	$96p_3 + 144p_4$	$24CO + 24C$				
4:6	$tC_{600}$	720	3600	$(1200 + 2400)p_3$	$600O + 120I$				
3:6	$tC_{120}$	1200	3600	$2400p_3 + 720p_5$	$120ID + 600T$				
3:6		30	60	$20p_3 + 20p_6$	$10tT$				
3:6		288	576	$192p_3 + 144p_8$	$48tC$				
3:6		20	60	$40p_3 + 30p_4$	$10T + 20P_3$				
3:6		144	576	$384p_3 + 288p_4$	$48O + 192P_3$				
3:6		$n^2$	$2n^2$	$n^2p_4 + 2np_n$	$2nP_n$				
5:8	$S_5^2$	20	90	$120p_3$	$30T + 30O$	$12tC_5$			
6:8	$HM_5$	16	80	$160p_3$	$(80 + 40)T$	$16C_5 + 10C_{16}$			
4:8	$S_5^1$	15	60	$(20 + 60)p_3$	$30T + 15O$	$6C_5 + 6tC_5$			
4:8	$Cr_5^1$	40	240	$(80 + 320)p_3$	$160T + 80O$	$32tC_5 + 10C_{16}$			
4:8	$Cr_5^2$	80	480	$(320 + 320)p_3$	$80T + 200O$	$32tC_5 + 10C_{24}$			
7:10	$V_{72}$	72	720	$2160p_3$	$2160T$	$432C_5 + 270C_{16}$	$54HM_5$		
6:10	$HM_6$	32	240	$640p_3$	$(160 + 480)T$	$192C_5 + 60C_{16}$	$32S_5 + 12HM_5$		
8:10	$V_{27}$	27	216	$720p_3$	$1080T$	$216C_5 + 432C_5$	$72S_5 + 27Cr_5$		
10:12	$V_{56}$	56	756	$4032p_3$	$10080T$	$12096C_5$	$(2016 + 4032)S_5$	$576S_6 + 126Cr_6$	
8:12	$V_{126}$	126	2016	$10080p_3$	$20160T$	$(4032 + 12096)C_5$	$4032S_5 + 756Cr_5$	$576S_6 + 56V_{27}$	
6:12	$V_{576}$	576	10080	$40320p_3$	$(30240 + 20160)T$	$16128C_5 + 7560C_{16}$	$2016S_5 + 2268HM_5$	$126HM_6 + 56V_{72}$	
8:14	$V_{5160}$	2160	69120	$483840p_3$	$1209600T$	$(241920 + 967680)C_5$	$483840S_5 + 60480Cr_5$	$138240S_6 + 6720V_{27}$	$17280S_7 + 240V_{126}$
12:14	$V_{540}$	240	6720	$60480p_3$	$241920T$	$483840C_5$	$483840S_5$	$(69120 + 138240)S_6$	$17280S_7 + 2160Cr_7$

T . . .	,,	tetrahedron,
C	,,	hexahedron (cube),
O	,,	octahedron,
C <sub>5</sub> . . .	,,	fourdimensional five-cell,
C <sub>16</sub>	,,	,,          sixteen-cell,
C <sub>24</sub>	,,	,,          twenty four-cell,
S <sub>n</sub>	,,	n-dimensional simplex,
Cr <sub>n</sub>	,,	,,          cross polytope.

The cases in which we have to deal with a half characteristic are also indicated in this table. So e.g. the first polytope of the table is limited by equilateral triangles of two different kinds, presenting themselves in the numbers 10 and 20.

*Meppel*, June, 1912.

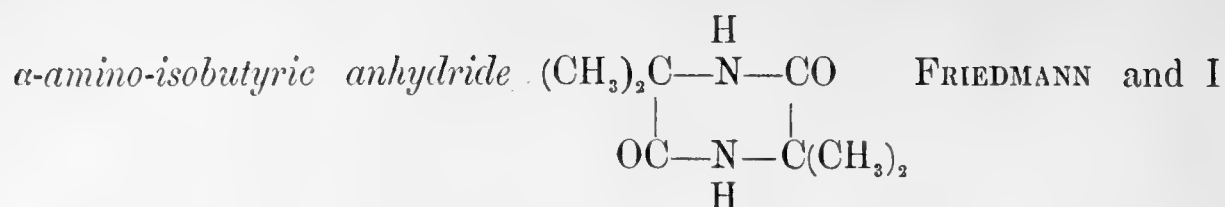
**Chemistry.** — “*Contribution to the knowledge of the direct nitration of aliphatic imino compounds*”. By Prof. A. P. N. FRANCHIMONT and Dr. J. V. DUBSKY.

In the January meeting 1907 I had the honour to give a survey of the action of absolute nitric acid on saturated heterocyclic compounds whose ring consists of C and N atoms. This originated in the fact observed and described by Dr. DONK, that the so-called

*glycocollanhydride* 
$$\begin{array}{c} \text{H} \\ | \\ \text{H}_2\text{C}-\text{N}-\text{CO}, \\ | \qquad \qquad | \\ \text{OC}-\text{N}-\text{CH}_2 \\ | \\ \text{H} \end{array}$$
 in which the group NH is placed

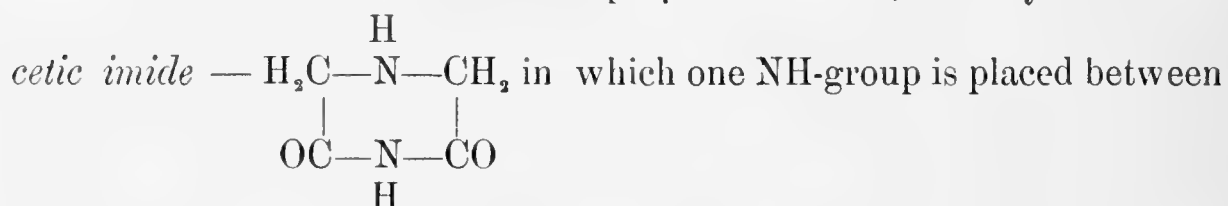
between CO and CH<sub>2</sub>, nitrated with difficulty, with much more difficulty than I had expected because a number of other heterocyclic compounds with rings of five or six atoms in which the group NH is placed in the same manner may be readily nitrated with absolute nitric acid at the ordinary temperature. This was not the case here; only a treatment of the nitrate with acetic anhydride or, as I showed with Dr. FRIEDMANN, of the glycocoll anhydride with acetic anhydride and nitric acid gave a mono- and a dinitroderivative.

With the so-called alanine anhydride 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{HC}-\text{N}-\text{CO} \\ | \qquad \qquad | \\ \text{OC}-\text{N}-\text{CH} \\ | \qquad \qquad | \\ \text{H} \qquad \qquad \text{CH}_3 \end{array}$$
 and with the



found something similar, with this understanding, however, that the nitration always took place with more difficulty, which can be attributed to sterical influence.

At the same meeting, I also called attention to the fact previously noticed by me that the group NH placed in a ring between two groups CO cannot be nitrated with absolute nitric acid, neither when it is placed between two saturated hydrocarbon groups. The expectation that one of the eleven isomers of the so-called glycoll anhydride which Dr. JONGKEES had prepared for me, namely *iminodiacetic imide*



two CO-groups and the other one between two CH<sub>2</sub>-groups, would not be capable of direct nitration by absolute nitric acid, was not realised in so far that it appeared indeed to give a nitroderivative but with some properties differing from those observed up to the present with nitramines and nitramides, so that it was questionable whether the nitrogroup is attached to the nitrogen or to the carbon.

Owing to the peculiar properties of the nitroderivative the chance of answering that question in a direct manner, for instance by reduction to hydrazine, was but a very slight one.

Moreover, the starting material, the imide, is obtained with difficulty and then only in small yield so that a great economy is necessary in the research. Two indirect ways could, however, be pursued, namely by starting from substances in which either the hydrogen at the N, or that at the C is replaced by other groups and to test these compounds  $\text{RN}(\text{CH}_2-\text{CO})_2\text{NH}$  and  $\text{HN}(\text{C}(\text{R})_2-\text{CO})_2\text{NH}$  as to their behaviour on nitration.

The last way is undoubtedly the best although even there we may meet with difficulties, for instance a difficult nitration owing to sterical hindrance as has already been demonstrated by me and FRIEDMANN.

Of the first process a few examples will be given here, namely acetyl and methyl derivatives, which, however, do not justify a final conclusion. The surmise that the NO<sub>2</sub>-group is placed at the N can be supported somewhat by the results of the nitration of the



acyclic compounds from which the imide is derived, such as iminodiacetonitrile, iminodiacetic acid, its ester and imide. This at the same time also furnishes a contribution to our knowledge of the nitration of acyclic imino compounds from which it is again evident that the nitration of one NH-group placed between two  $\text{CH}_2$ -groups (residues of saturated hydrocarbons) depends also on other constituents attached to these hydrocarbon residues.

The results obtained are as follows :

*Iminodiacetonitrile*  $\text{HN}(\text{CH}_2\text{CN})_2$  yields with ordinary nitric acid a nitrate in beautiful glittering needles which melt at  $138\text{--}140^\circ$  with decomposition. The formula was determined by analysis and titration of the nitric acid. It is readily soluble in cold water, soluble in hot methyl alcohol, ethyl alcohol and benzene. On slowly cooling a hot alcoholic solution it yields very beautiful crystals. If this nitrate is dissolved in absolute nitric acid (which is accompanied by a slight evolution of heat) and the acid is allowed to evaporate in vacuo over lime, the residue when triturated with absolute alcohol gives a crystal-paste which, after being dried and recrystallised from dry benzene, forms splendid snow-white needles melting at  $100\text{--}101^\circ$ . Their analysis points to the nitro-derivate  $\text{NO}_2\text{N}(\text{CH}_2\text{CN})_2$  *nitro-iminodiacetonitrile*. It gives the reaction of the nitramines with zinc and an acetic acid solution of  $\alpha$ -naphthylamine. On warming with water decomposition sets in.

*Iminodiacetic acid*  $\text{HN}(\text{CH}_2\text{CO}_2\text{H})_2$  gives a nitrate already described in 1865 by HEINTZ. When this nitrate is dissolved in absolute nitric acid and evaporated in vacuo over lime it is recovered unchanged. It is insoluble in ether, benzene and acetic ether. If, however, the nitric acid solution is heated to boiling a nitroderivative  $\text{NO}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$  *nitroiminodiacetic acid* is formed, which is left behind after evaporation of the nitric acid in vacuo over lime. It is soluble in methyl and ethyl alcohol in acetone and acetic ether, also in cold water. Crystallised from acetic ether it forms broad, flat needles mutually joined like a fan. Its melting, or rather decomposition point appears to lie at about  $153^\circ$ . Its aqueous solution is strongly acid and gives the above nitramine reaction. A neutral potassium salt was prepared which readily crystallises on addition of absolute alcohol to the watery solution; it is decomposed at about  $195^\circ$  with explosion. The acid potassium salt which is not easily soluble in alcohol and yields beautiful crystals was also prepared. From the ethyl ester of iminodiacetic acid described by Mr. JONGKEES there was also prepared a nitrate, which is very little soluble in alcohol and crystallises in silky needles, which melt at

198—199°. By treating this nitrate, in the manner described, with absolute nitric acid in the cold it is recovered unchanged but if the solution is heated to boiling the nitroderivative  $\text{NO}_2\text{N}(\text{CH}_2\text{CO}_2\text{CH}_3)_2$  is formed which is not, or but little, soluble in cold water so that it may be precipitated by pouring the nitric acid solution into cold water. From acetic ether, in which it is soluble, it is obtained in silky delicate scales which melt at  $63^\circ.5$ .

*Iminodiacetamide*  $\text{HN}(\text{CH}_2\text{—CONH}_2)_2$  gave with one mol. of  $\text{NO}_3\text{H}$  a nitrate which was obtained from the aqueous solution, by addition of absolute alcohol, in beautiful lustrous leaflets which melt at  $206^\circ$  with decomposition. If this nitrate is placed in absolute nitric acid, an evolution of gas takes place after a short time, as in the case of all amides of  $\text{N}_2\text{O}$ ; when this has ceased, or has been accelerated by warming, the nitro-iminodiacetic acid is obtained.

*Iminodiacetimide*  $\text{HN}(\text{CH}_2\text{CO})_2\text{NH}$ , which was made according to the directions of JONGKEES, also gave compounds with acids. We prepared: (1) the  $\text{HCl}$  compound in lustrous, beautiful crystals which are decomposed on heating above  $180^\circ$ ; (2) the  $\text{NO}_3\text{H}$  compound, also white crystals with a strong lustre, which when heated above  $180^\circ$ , are decomposed and turn a bluish-green. Both compounds contain one mol. of acid.

When iminodiacetimide or its nitrate is dissolved in absolute nitric acid and the solution evaporated in vacuo over lime a crystal-cake is obtained which may be recrystallised from boiling dry chloroform in which it is very little soluble. It then forms beautiful colourless needles which have the empirical composition of a mononitroderivative. This *nitroiminodiacetimide*  $\text{NO}_2\text{N}(\text{CH}_2\text{CO})\text{NH}$  spontaneously turns a dark blue, especially in not quite dry air and its aqueous solution on warming first turns green, then blue and deposits an almost black amorphous substance soluble only in strong sulphuric acid with an indigo-blue colour.

In order to render it more probable still that the nitro-group is attached to the nitrogen situated between the  $\text{CH}_2$ -groups, the *acetyliminodiacetimide*  $\text{CH}_3\text{CON}(\text{CH}_2\text{CO})_2\text{NH}$  was prepared first of all by subliming in vacuo acetyliminodiacetamide, which according to JONGKEES decomposes at  $203^\circ$ . On recrystallising the sublimate from methylalcohol splendid small crystals were obtained which melt at  $167\text{—}168^\circ$  and according to analysis, have the empirical composition of acetyliminodiacetimide. They are insoluble in benzene, petroleum ether and acetic ether. The same substance was prepared by boiling iminodiacetimide with acetic anhydride. This acetyl derivative was dissolved in absolute nitric acid and the solution evaporated in vacuo

over lime. The residual crystalline mass, after being recrystallised from methyl alcohol, proved to consist mainly of unchanged acetyl derivative. The mother liquor, however, exhibited colour phenomena which may raise a suspicion that a small fraction of the acetyl group has been replaced by the nitro-group.

Finally, also a few derivatives of *methyliminodiacetic acid*  $\text{CH}_3\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$  were made, in which the hydrogen atom of the NH-group which is placed between 2  $\text{CH}_2$  has been replaced by methyl. First of all the *diamide* by acting on the methyl ester of the said acid for some time, with  $\text{NH}_3$  in methyl alcoholic solution. This diamide  $\text{CH}_3\text{N}(\text{CH}_2\text{CONH}_2)_2$  forms beautiful, large crystals melting at  $162\text{--}163^\circ$ ; it is readily soluble in cold water, methyl- and ethyl alcohol, very little so in acetic ether, acetone, ether, petroleum ether, chloroform and benzene. It was recrystallised from boiling methyl alcohol.

From the diamide the *imide* was prepared by sublimation under a pressure of 17—18 m.m. at  $200\text{--}220^\circ$ . The *methyliminodiacetimide*  $\text{CH}_3\text{N}(\text{CH}_2\text{CO})_2\text{NH}$  thus obtained was first recrystallised from boiling acetic ether in which the amide is practically insoluble, then from boiling acetone and finally from a little boiling methyl alcohol. It then forms white, glittering crystals which melt at  $106^\circ$ . This imide gives crystallised compounds with one mol. of  $\text{HCl}$  or  $\text{NO}_2\text{H}$ . The first is decomposed by heating above  $235^\circ$ ; the second by heating above  $130^\circ$ ; treated with absolute nitric acid an oxidation seems to take place slowly at the ordinary temperature, at least after being some time in vacuo over lime a decidedly strong evolution of red fumes took place and from the residual swollen mass no well-defined product could, as yet, be isolated.

Although the question as to the position of the nitro-group in nitroiminodiacetimide is not yet quite solved, as this position will be determined fully only then when the analogous isobutyric acid derivative  $\text{HN}(\text{C}(\text{CH}_3)_2\text{CO})_2\text{NH}$  has also been tested as to its behaviour on nitration, yet it has been rendered very probable by the results obtained, the publication of which was rendered desirable owing to to the departure of Dr. DUBSKY.

The direct nitration capacity of the above acyclic aliphatic amino-compounds, also the differences in the readiness of this nitration point to a connection with what has been found in the case of aromatic N-compounds where the nitration capacity, or otherwise the formation of nitramines by direct nitration, has been first shown by VAN ROMBURGH.

This connection is quite in harmony with what I have demonstrated

previously as to the direct nitration capacity of aliphatic carbon compounds, by nitrating malonic acid and its esters, methylenetricarboxylic ester etc. from which it follows that the direct nitration capacity is caused by the adjacency of so-called negative groups of definite strength.

In this manner were also discovered the aliphatic nitramines and nitramides, by nitrating the amides wherein occurs also a negative group and it now appears that an aliphatic secondary amine (dimethylamine) may also undergo direct nitration when in the alkyl groups are present the group CN or CO<sub>2</sub>H, so distinctly negative groups.

I, therefore, put to myself the question whether the phenyl or nitrophenyl-group would also be able to give the same result as CN or CO<sub>2</sub>H. This, however, does not seem to be the case, for dibenzylamine HN(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> yielded only dinitrodibenzylamine nitrate, but no nitramine on boiling with absolute nitric acid.

The ready nitration capacity of iminodiacetonitrile and of iminodiacetic acid and its derivatives is striking especially when we compare it with that of other substances as shown in the subjoined list.

CH <sub>3</sub> .NH.CH <sub>3</sub>	not	CN.CH <sub>2</sub> .NH.CH <sub>2</sub> .CN	readily
CH <sub>3</sub> .NH.CO.CH <sub>3</sub>	readily	CO <sub>2</sub> H.CH <sub>2</sub> .NH.CH <sub>2</sub> .CO <sub>2</sub> H	readily
CH <sub>3</sub> .CO.NH.COCH <sub>3</sub>	readily	CO <sub>2</sub> .CH <sub>3</sub> .CH <sub>2</sub> .NH.CH <sub>2</sub> .CO <sub>2</sub> .CH <sub>3</sub>	readily
CH <sub>3</sub> .NH.CO <sub>2</sub> CH <sub>3</sub>	readily	C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )CH <sub>2</sub> .NH.CH <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	not
CH <sub>3</sub> .CO.NH.CO <sub>2</sub> CH <sub>3</sub>	readily	C <sub>6</sub> H <sub>2</sub> (NO <sub>2</sub> ) <sub>3</sub> .NH.CH <sub>3</sub>	readily
CH <sub>3</sub> .CO <sub>2</sub> .NH.CO <sub>2</sub> CH <sub>3</sub>	not	C <sub>6</sub> H <sub>2</sub> (NO <sub>2</sub> ) <sub>3</sub> .NH.C <sub>6</sub> H <sub>2</sub> (NO <sub>2</sub> ) <sub>3</sub>	not

**Biochemistry.** — “*A biochemical method of preparation of l-Tartaric acid.*” By Prof. J. BÖESEKEN and Mr. H. J. WATERMAN. (Communicated by Prof. BEIJERINCK).

In our investigations on the assimilation of carbon nutriment by different kinds of mould it was found necessary to get some more information as to the manner in which the carbon was retained in the body of the plant either temporarily or permanently.

For this purpose one of us (H. J. W.) carried out a large number

of carbon determinations of the mould that formed on a definite organic compound used as exclusive carbon nutriment; while at the same time the amount of unattacked substance in the nutrient base was determined. The further particulars of this research will be communicated by him elsewhere, when the significance of the survey thus obtained of the course of the plastic equivalent or *assimilation quotient of the carbon*<sup>1)</sup> will also be explained: here we will call attention to some observations on the growth of *Aspergillus niger* and *Penicillium glaucum* on the tartaric acids.

*Aspergillus niger* grew hardly at all on *l*-tartaric acid, but very well on the *d*-acid, so that a 2% solution of the latter provided with the necessary inorganic nutriment was, after the lapse of six days used up by the mould. A 4% solution of uvic acid provided with 0.15%  $\text{NH}_4\text{NO}_3$ , 0.15%  $\text{KH}_2\text{PO}_4$  and 0.06%  $\text{MgSO}_4$  and inoculated in the usual manner with *Aspergillus niger* and cultivated at 33°—34° gave after six days a maximum *l*-rotation; this then began to decrease slowly, showing that the *l*-tartaric acid also gets consumed.

This maximum rotation observed with the saccharimeter of SCHMIDT and HAENSCH for white light in a 20 cm. tube, amounted to  $-1^{\circ}0$  corresponding with a solution of about 1,2% *l*-tartaric acid.

As a 4% solution of uvic acid can only give at most a 1.88% solution of *l*-tartaric (on account of the disappearance of the *d*-acid and the water of crystallisation of the uvic acid) this maximum rotation corresponds with a yield of fully 60%.

In order to isolate the *l*-tartaric acid the liquid after removal of the film of mould, was precipitated with lead acetate. The precipitate, after being washed was decomposed with hydrogen sulphide and the filtrate evaporated.

From 4 grams of uvic acid was obtained 0.8989 gram of *l*-tartaric acid = 56%.

The acid crystallises readily.

0.100 gram consumed 8,6 cc. of baryta water of which 4.66 were equivalent to 0.100 gram of salicylic acid: Mol. Weight = 149.3 (calculated 150)

0.2719 gram was dissolved in 50 cc. Polarisation in a 40 cm. tube =  $-0^{\circ}8$ , that is, for a solution in a 20 cm. tube =  $-1^{\circ}5$ , while a 2% solution of pure *d*-acid gave  $+1^{\circ}6$ .

As a part of the *l*-acid is consumed and as this is connected with

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<sup>1)</sup> Compare WATERMAN, Mutation with *Penicillium glaucum* etc. These Proc. 29 June 1912, p. 124.

the increase of the mould material, it is desirable not to subject <sup>1)</sup> large quantities of uvic acid to this operation all at once, but to distribute it into a number of small flasks (containing not more than 50 cc.). Operating in this manner we prepared from 40 grams of uvic acid, distributed into 20 flasks, nearly 9 grams of pure *l*-tartaric acid.

The question, which is more of a biological than of a chemical nature, how the *l*-tartaric acid is decomposed, could be answered by the determination of the above quoted assimilation quotient of the carbon, in that sense that it takes part, in the same degree as the *d*-acid, in the construction of the organism. This could not be proved in a direct manner, because the pure *l*-acid promoted the growth of the inoculating material too slowly, but it could be determined from the values obtained in the growth on uvic acid compared with that of *d*-tartaric acid.

The *l*-acid is evidently attacked only a little slower. If we mix *d*-acid with uvic acid this will not much affect the absolute consumption of the *l*-acid because the total amount of mould material formed in the same time will be approximately the same. As, however, we can only subject to the operation a solution not exceeding 6 ‰, the quantity of *l*-tartaric acid is smaller from the commencement and the yield will have to be low. If, for instance, we mix 1½ gram of *d*-tartaric acid with ½ gram of uvic acid, practically no *l*-acid will be left when all the *d*-acid has disappeared.

These experiments with *Aspergillus* were carried out in conjunction with others, because we had noticed that *Penicillium glaucum*, which was used for many of our observations exhibited towards the tartaric acids a but little pronounced power of selection. This will be seen at once from the subjoined table.

The three acids behave nearly similar in regard to a same *Penicillium* culture; only during the first days the growth on the *l*-acid is somewhat less than on the two others.

It seems remarkable that, in consequence of the great concentration of the hydrogen ions, the retardation which in a 2 ‰ solution of *l*- and *d*-acid is very plainly perceptible after six days <sup>2)</sup> does not set in at all with the anti-acid. This is quite in harmony with the smaller dissociation constant of this acid <sup>3)</sup> owing to which, in a

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<sup>1)</sup> When using larger flasks, the surface in regard to the capacity is as a rule more unfavourable than when small flasks are used, so that the aeration becomes insufficient.

<sup>2)</sup> BÖESEKEN and WATERMAN. These Proc. 30 March 1912, p. 1112.

<sup>3)</sup> BISCHOFF and WALDEN. Ber. D. Ch. G. 22, 1819 (1889).

TABLE I.

Development of *Penicillium glaucum* in 50 cc. tapwater, provided with 0.05 %  $\text{NH}_4\text{Cl}$ , 0.05 %  $\text{KH}_2\text{PO}_4$  and 0.02 %  $\text{MgSO}_4$ .  
 $T = 21^\circ$ .

N <sup>o</sup> .	added acid in mg.	Development in stated number of days.		
	<i>d</i> -tartaric acid	2	4	6
1	50	+	+>	++
2	100	+	+>	++
3	300	+	+>	++>
4	500	+	+ } slight	++<
5	1000	+		+
	<i>l</i> -tartaric acid			
6	50	+	+ } slight	++<
7	100	+		++<
8	300	+		++
9	500	?	+	++<
10	1000	?	+	+>
	Antitartaric acid <sup>1)</sup>			
11	50	+	+	++
12	100	+	+>	++>
13	300	+	+	++>
14	500	+	+	++
15	1000	+	+>	++

2 % solution thereof, the harmful concentration of the H-ions for *Penicillium* is not yet reached.

For the rest, these small differences in growth at lower concentrations are somewhat unexpected because the specific character of the two anti-podes has been determined by PASTEUR first of all with *Penicillium glaucum*. But it may be very well assumed that the

<sup>1)</sup> *Aspergillus niger* gives practically no growth on antitartaric acid.

organism used by us has been another form than that employed by PASTEUR in his classic experiment and the continued investigations of one of us <sup>1)</sup> (H. J. WATERMAN) have exactly demonstrated that the phenomena of growth are dependent in a high degree on the variation.

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**Chemistry.** — “*On a method for a more exact determination of the position of the hydroxyl groups in the polyoxycompounds*”.  
(4<sup>th</sup> Communication on the configuration of the ring systems).<sup>2)</sup>  
By Prof. J. BÖESEKEN. (Communicated by Prof. A. F. HOLLEMAN).

The investigations as to the action of the polycompounds on the conductivity of boric acid were started to furnish a contribution to our knowledge as to the situation of the carbon atoms, and the groups attached thereto, in benzene.

This object has been attained to a certain extent, but, in addition, the measurements have also taught us something about the position of the hydroxyl groups in the saturated polyvalent alcohols.

The influence of polyoxycompounds and boric acid on each other has been known for a long time.

So, for instance, the increase of the acidic properties of boric acid by means of glycerol was made use of in the titration of that acid and, reversely, the large increase in rotation exerted by boric acid on mannitol went to demonstrate that this polyatomic alcohol was indeed optically-active <sup>3)</sup>. These few empirical data were very considerably added to by G. MAGNANINI <sup>4)</sup>; at the same time an experimental foundation was given to the surmise that these phenomena might be due to the formation of compounds.

He demonstrated that mannitol strongly increased the electric conductivity power of boric acid and that, although to a less extent, this was also the case with oxy-acids such as tartaric acid, salicylic acid, lactic acid, glycerine acid, gallic acid, mandelic acid and glycollic acid. He thus proved the formation of complex ions, consequently of a chemical combination between the two components.

VAN 'T HOFF <sup>5)</sup>, on account of these investigations, was of opinion

1) H. J. WATERMAN. These Proc. 29 June 1912, p. 124.

2) Recueil 30, 392; 31, 80 and 86.

3) VIGNON. Ann. Chim. Phys. 5e S. II 433. (1874).

4) Gazz. chim. 20, 428; 21, II, 134, 215. Zeitschr. phys. Chem. 6. 58.

5) Lagerung der Atome im Raume. 3e Ed. p. 90.



that a compound can only then be formed when the conditions are favourable for the formation of a 5-ring (and eventually of a 6-ring). A substance like mannitol might then unite readily with one or more mols. of boric acid, because the position of the hydroxyl groups would favour the formation of 5- or 6-rings.

In the case of a hexatomic alcohol like mannitol, the conditions for the ring formation are, however, probably favourable, because to each carbon group is attached a hydroxyl group and because of the very great probability that two of these with the two carbon atoms attached thereto, are situated at the same side and in the same plane; and this especially because it is a saturated non-cyclic substance.

It occurred to me that a further study of the influence of these compounds on boric acid might become of more importance still, if the more simple alcohols were chosen for that purpose.

Now, with the polyoxyderivatives of benzene the conditions are exceedingly simple.

When in the benzene derivatives the six carbon atoms with the groups attached thereto, are situated in one plane, the *orthodioxy*-compounds only (eventually also the *ortho*oxyacids have a configuration that offers the best chances for the formation of the said cyclic systems.

In fact, the measurements carried out by myself and A. VAN ROSSEM (l. c.) have shown that of the polyoxyderivatives of benzene only the *ortho*compounds exert a very great positive influence on the conductivity of boric acid.

The specific conductivity of  $\frac{1}{2}$  mol. solution of this acid at  $25^{\circ}$  is increased:

by $\frac{1}{2}$ mol. pyrocatechol	from $25.7 \times 10^{-6}$	to $553.2 \times 10^{-6}$
„ $\frac{1}{2}$ „ pyrogallol. . . . .		$608.9 \times 10^{-6}$
„ $\frac{1}{32}$ „ pyrocatechol . . . . .		$116 \times 10^{-6}$
„ $\frac{1}{32}$ „ pyrogallol . . . . .		$131 \times 10^{-6}$
„ $\frac{1}{32}$ „ 1.2-dioxynaphtalene . . . . .		$112 \times 10^{-6}$

(measured by Mr. J. D. Rurs)

on the other hand, the *meta*- and *para*derivatives exerted an insignificant negative influence. The spec. conductivity was lowered:

by $\frac{1}{2}$ mol. resorcinol	from $25.7 \times 10^{-6}$	to $25.0 \times 10^{-6}$
„ $\frac{1}{2}$ „ hydroquinone . . . . .		$24.3 \times 10^{-6}$
„ $\frac{1}{8}$ „ phloroglucinol . . . . .		$24.8 \times 10^{-6}$

Gallic acid and protocatechuic acid also suffer a considerably larger increase in conductivity by addition of boric acid than would agree with this acid's own conductivity.

$\frac{1}{8}$ mol. protocatechuic acid had at 25° a specific conductivity	$= 703.1 \times 10^{-6}$
$\frac{1}{2}$ mol. boric acid	$= 25.7 \times 10^{-6}$
Found a conductivity of the mixture	$= 847.7 \times 10^{-6}$
	Increase $= 118.9 \times 10^{-6}$
<hr/>	
$\frac{1}{8}$ mol. of gallic acid had at 25° a spec. conductivity	$= 750.7 \times 10^{-6}$
$\frac{1}{2}$ „ of boric acid	$= 25.7 \times 10^{-6}$
Found for the mixture	$= 917.6 \times 10^{-6}$
	Increase $= 141.2 \times 10^{-6}$
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From this influence on the conductivity we may conclude that with the polyoxybenzene derivatives an important reaction only then takes place when the hydroxyl groups are situated in the *ortho*-positions in regard to each other,

Of a specific aromatic influence there can be no question because it would then be difficult to understand why resorcinol, hydroquinone and phloroglucinol do not exert an increasing action whereas mannitol, pentaerythrol and glycerol do increase the conductivity (MAGNANINI, BÖESEKEN and VAN ROSSEM l. c.).

We are constrained, as stated above, to look for the cause in the favourable situation of the hydroxyl groups in regard to the boric acid molecule.

Now, the peculiar property of pyrocatechol and other orthodioxy- (and also of amido-oxy and diamido-) compounds of benzene and other ring systems to readily absorb another atom and to form with this, as a rule, very stable compounds has been known for a long time.

This is attributed to the exceedingly ready 5-ring formation, therefore to the favourable position of the *ortho*-placed groups.

Without troubling, provisionally, about the configuration of the compounds formed between boric acid and the polyoxyderivatives, we may take it as very probable that an analogous cause determines their origin.

The importance of demonstrating the influence of the polyoxy-compounds on the conductivity of boric acid is not related to the fact itself but lies in the sensitiveness of the method and its simple application.

It enables us to announce the formation of compounds without having to isolate the same and even more: *from the degree of influence we can draw important conclusions as to the position of the hydroxyl groups in the original polyoxycompound.*

If, for instance, we find that the increase of the specific conductivity at 25° caused by:

$\frac{1}{2}$ n. glycol	on $\frac{1}{2}$ n. boric acid =	$4.9 \times 10^{-6}$
$\frac{1}{2}$ n. glycerol	„ . . . . . =	$8.7 \times 10^{-6}$
$\frac{1}{2}$ n. pentaerythrol	„ . . . . . =	$231.2 \times 10^{-6}$
$\frac{1}{2}$ n. pyrocatechol	„ . . . . . =	$514.1 \times 10^{-6}$
$\frac{1}{2}$ n. dulcitol	„ . . . . . =	$717 \times 10^{-6}$

we may conclude therefrom that in pentaerythrol, at least two of the hydroxyl groups are situated rather favourably, but not by a long way so as in the case of pyrocatechol; that in dulcitol more than *one* pair of hydroxyl groups exert an influence on the boric acid; that in glycol, they are very unfavourably situated and that they are also unfavourably situated in glycerol although three of them are present. This is shown in a still more striking manner when we compare the trivalent pyrogallol with glycerol at a somewhat greater concentration of the alcohol:

1 n. pyrogallol on $\frac{1}{2}$ n. boric acid =	$911.3 \times 10^{-6}$
1 n. glycerol . . . . . =	$12.9 \times 10^{-6}$

In the determination of the influence exerted on the conductivity we possess a very simple and sensitive method to get some information as to the situation of the hydroxyl groups in regard to each other without strongly attacking the molecule and so disturbing the existing equilibrium.

In consequence of the preceding we submit the following suppositions:

1. If the hydroxyl groups, as in pyrogallol or in pyrocatechol, are situated in the same plane and at the same side of the carbon atoms to which they are attached and if there is no entering atom as in the case of resorcinol, hydrochinone or phloroglucinol, the influence is very great.

2. This influence becomes less when the OH-groups are leaving this favourable position.

The simple glycols as yet investigated by us: aethylene glycol, pinacone, propanediol 1,3, butanediol 1,4<sup>1)</sup>, do not increase the conductivity of boric acid.

We surmise that the hydroxyl groups in these molecules repel each other and then, in consequence of the mobility of the saturated molecule, get situated as far as possible from each other, still in the same plane but at the opposite side of the carbon atoms to which they are attached.

We will see whether a more extensive experimental material confirms these suppositions.

<sup>1)</sup> Butanediol (1.4) can be prepared very readily by reduction of succinidiethyl ester according to the directions given by HARRIES for the preparation of methyl (2) butanediol (1.4) from pyrotartaricdiethyl ester.

The influence of glycerol is certainly in harmony with these views. As we have stated this influence is very slight; two of the OH-groups are therefore, most likely, not situated so favourably as in pyrocatechol. But still they are not situated so unfavourably as in the simple glycols and this cannot be otherwise, for even when the three OH-groups repel each other as far as possible the situation of these groups viewed two by two must still be more favourable than in the said bivalent alcohols.

The fact that on the other hand the position of the hydroxyl groups in pyrocatechol and in dioxynaphtalene is so particularly favourable must be attributed to the ring-system of the benzene, which forces them to remain in the plane of the ring and at the same, or outer, side.

The fact that, according to MAGNANINI's measurements, the  $\alpha$ -oxy-acids and salicylic acid affect the conductivity of boric acid positively, points to a position of the hydroxyl groups, in regard to each other, which is more favourable than in the glycols. This is very comprehensible when we consider that the OH-group of the  $\alpha$ -carbon atom finds at the other side of the acid OH-group of the carboxyl group an oxygen atom, and not the hydrogen atoms of the glycols.

If the number of hydroxyl groups in saturated compounds is greater than two, it is obvious that the chances of a favourable position increase and in harmony therewith we find that erythrol exerts a stronger influence on the conductivity of boric acid than glycerol and that the action of mannitol and dulcitol is more important still.

For  $\frac{1}{2}$  mol. of the alcohols on  $\frac{1}{2}$  mol. of boric acid was found:  
 $K \times 10^{-6} =$

Glycerol	Erythrol	Mannitol	Dulcitol
8.7	64.1	685	717

In the case of these saturated polyalcohols it is, at the present, still somewhat difficult to point out the most probable position of the hydroxyl groups by means of a determination of the influence exerted on the conductivity.

This is much more easy in the case of cyclic systems where the mobility of the molecule has been lessened to a considerable extent by the closing of the ring thus causing the position of the groups to become much more defined. We have already made use of this property in criticising the action of the polyoxycompounds of benzene; but the action of *sucrose* is also that which may be expected from this molecule.

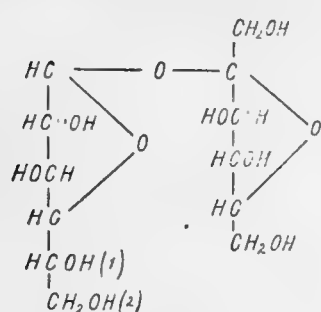
The influence of sucrose on the conductivity of boric acid is very trifling, and reversely, also that of boric acid on the rotatory power of sucrose.

The change of  $\frac{1}{34.2} N$  sucrose to  $\frac{1}{2} N$  boric acid  $= \pm 0$

„ „ „  $\frac{1}{3.42} N$  „ „ . . . . .  $= -1 \times 10^{-6}$

„ „ „  $\frac{1}{1.71} N$  „ „ . . . . .  $= -3 \times 10^{-6}$

The change in the rotation for these concentrations kept below  $0,13^\circ$  and like that of the conductivity was exceedingly small indeed.



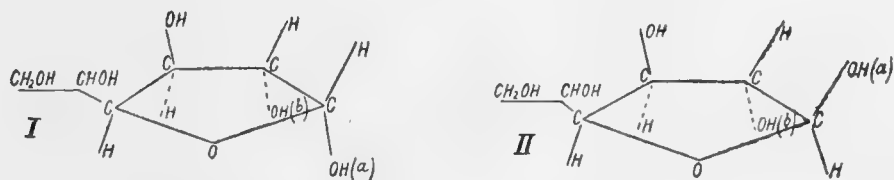
If now we observe the subjoined symbol of sucrose in space, which is considered by TOLLENS and E. FISCHER<sup>1)</sup> as the most probable one, we notice that of the eight hydroxyl groups only those indicated by (1) and (2) can have a favourable position, that is to say, in the same plane and at the same side of the carbon

atoms to which they are attached and undisturbed by other atoms.

It was, however, to be expected that these two OH-groups will *not* be situated favourably, for they possess a freedom of motion analogous to that in the simple glycol and if in the latter the OH-groups repel each other it would be difficult to understand why they should not do so in the sucrose molecule.

The almost complete indifference of sucrose towards boric acid (and probably towards many other compounds) now finds in its configuration a very simple explanation.

These observations thus confirm the configuration of the sucrose as well as the value of the process for the more exact determination of the hydroxyl groups of organic compounds. I have been able to employ the method for determining the configuration of  $\alpha$ - and  $\beta$ -dextrose.



It is known that the above configurations are now imputed to both these isomers. If this be correct they must behave differently in regard to boric acid.

<sup>1)</sup> E. FISCHER, B 45, 461 (1912).

One of them, represented by (I) must, in consequence of the favourable position of the hydroxyl groups (*a*) and (*b*), influence the conductivity more forcibly than the other one and because in aqueous solution they are converted into each other up to a definite equilibrium, the conductivity must decrease until this equilibrium-mixture is attained.

In the other represented by II the conductivity must increase until the same limit value is attained.

The preliminary measurements executed by Mr. C. E. KLAMER now have led to the result:

1. That  $\alpha$ -dextrose had, at  $25^\circ$ , a considerable positive influence on the conductivity.

2. That this decreased slowly so as to attain a definite limit value after 24 hours.

3. That the positive influence of  $\beta$ -dextrose (up to the present not obtained in a perfectly pure condition) was much slighter than that of  $\alpha$ -dextrose.

4. That it kept on increasing slowly to finally reach nearly, but not quite, the same limit value as in the case of the  $\alpha$ -dextrose.

After repeated recrystallisations the conductivity of a 6.5% solution of  $\alpha$ -dextrose at  $25^\circ$  was on an average  $5 \times 10^{-6}$ , of a 15% solution  $7 \times 10^{-6}$ , that of a 6.5% solution of  $\beta$ -dextrose obtained by recrystallisation from pyridine  $10 \times 10^{-6}$ , presumably it still contained a little pyridine.

The increase of the conductivity caused by a

$$\begin{array}{l} 6.5\% \alpha\text{-dextrose solution on } 2\frac{1}{2}\% \text{H}_3\text{BO}_3 = 42 \times 10^{-6} \\ \text{falling to } 35 \times 10^{-6} \end{array}$$

The increase of the conductivity caused by a

$$\begin{array}{l} 15\% \alpha\text{-dextrose solution on } 2\frac{1}{2}\% \text{H}_3\text{BO}_3 = 106 \times 10^{-6} \\ \text{falling to } 90 \times 10^{-6} \end{array}$$

The increase of the conductivity caused by a

$$\begin{array}{l} 6.5\% \beta\text{-dextrose solution on } 2\frac{1}{2}\% \text{H}_3\text{BO}_3 = 20 \times 10^{-6} \\ \text{rising to } 29 \times 10^{-6} \end{array}$$

Without anticipating the result of the final measurements with the sugars we may safely conclude that this method which, of course, is capable of extension in many directions can give us further data as to the more delicate structure of the molecules.

In other respects also, the formation of complex compounds of boric acid with organic polyoxycompounds is of great importance.

We know that boric acid is used as an antiseptic; this is based on the retarding action which this substance exerts on the growth of moulds.

According to the researches of H. J. WATERMAN and myself described in these Proc. (30 Dec. 1911 and 30 March 1912) retardation is usually associated with a strong solubility in fat or with a too large concentration of hydrogen ions.

Now, boric acid is much more readily soluble in water than in olive oil and is moreover an exceedingly feeble acid so that these two properties cannot, therefore, explain to us why boric acid so very much retards the growth of *penicillium glaucum* as we have indeed observed.

The formation of compounds with the polyalcohols which play such an important rôle in the living beings, compounds which can, moreover, be much more strongly acid than boric acid itself, offers a very simple explanation of the powerful action of this apparently so innocuous substance.

Under the influence of the development of the chemistry of the colloids, the origin of physiological processes has been perhaps searched for a little too much in purely physical phenomena: diffusion, change in surface tension, discharge of negative-charged colloids by positive ions and reversely, etc. Undoubtedly, all these actions play an exceedingly important rôle, but in many cases a chemical phenomenon is involved; it is like this with boric acid and so it will be, presumably, with the toxic action of many metals (I further refer to a communication from H. J. WATERMAN and myself in the "Folia microbiologica").

The question whether the strong action of some of the hydroxyl compounds is associated with an easy ring formation, as surmised by VAN 'T HOFF, has, as yet, been discussed by me only casually.

Last year, FOX and GAUGE (Trans. Chem. Soc. 1911, 1075) have succeeded in isolating mannitoboric acid and in preparing some of its salts, but as it appears from the analytical figures that there is present one molecule of water in excess of that required for the 5-ring closure, the configuration still remains uncertain.

As pyrocatechol causes a very strong increase of the conductivity I have endeavoured to obtain pyrocatecho-boric acid. Although we have not succeeded in doing so, we have yet managed to prepare a series of readily crystallizable complex salts some of which are characterised by a very slight solubility, so that they may, presumably, serve for the quantitative separation of boric acid.

A full description of these salts, also of the experiments mentioned above, which have been carried out mainly by Mrs. N. H. SIEWERTS VAN REESEMA, C. E. KLAMER and J. D. RUYS, will be given later.

Delft, May 1912.

Org. Chem. Lab. Techn. High School.

**Geology.** — G. A. F. MOLENGRAAFF: "*On recent crustal movements in the island of Timor and their bearing on the geological history of the East-Indian archipelago.*"

The occurrence of elevated coralreefs on the islands of the eastern portion of the East-Indian archipelago, amongst others on the island of Timor, has attracted the attention of many scientists, because it proves that in a geological sense not long ago, these islands have been considerably raised above the level of the sea.

The Timor-expedition<sup>1)</sup> particularly studied these elevated reefs and their results may throw some light on the question of the character and correlations of the recent crustal movements in the East-Indian archipelago.

The following brief remarks, therefore, are intended as introduction to the history of these reefs.

The strata of the island of Timor were greatly folded at a time, which is known to be post-eocene and pre-pliocene, but which cannot at present be more precisely defined. Among these strata besides schists of unknown age various formations ranging from the Permian to the Eocene are represented, the whole of which will be here indicated by the name of the Perm-Eocene-series or simply as the older formations.

This period of folding and tilting was most probably followed by a period of prolonged and considerable denudation, because it is observed that a later-tertiary formation of neogene age is found resting unconformably on the much denuded (peneplainized) older formations. The oldest strata of these neogene deposits consist of pure Globigerina-limestone, a pelagic sediment devoid of the elements of terrigenous origin, which must have been formed in an open sea far distant from the land.<sup>2)</sup>

From the time of deposition of the Globigerina-limestone important crustal movements had set in, which resulted in the forming of basins (graben), in which the soil was deposited slowly but continuously and thus filled up these true depressions<sup>3)</sup>.

<sup>1)</sup> Messrs. H. A. BROUWER, F. A. H. WECKHERLIN DE MAREZ OYENS and the author as leader, formed the Timor-expedition, during which geological explorations were made in the eastern half of the Netherlands-Timor in the years 1910—1912.

<sup>2)</sup> I am not inclined to regard this formation as a deep sea deposit, although it must have been formed in the open-sea far from the land, but believe, that it may have deposited under similar conditions as the white chalk of Europe, to which this late-tertiary Globigerina deposit bears petrologically a remarkable resemblance.

<sup>3)</sup> Only the most important of those graben or depressions, which have been of such vital importance in the development of the later-tertiary deposits, are mentioned in this paper:

As the German terms "graben" and "horsten" are frequently used in this paper,



Beyond the "graben", in the adjoining "horsten", a slow upheaval of the land took place, in consequence of which the sea became shallower thus causing the growth of coralreefs upon the Globigerina-limestone. Foraminifera are found abundantly in these reefs whose preliminary determination points to a probable miocene age, although such an assumption must be confirmed by further palaeontological examination. Sometimes small pebbles are found in these reefs and in places they pass into littoral conglomerates. It appears that coralreefs have been formed continuously during the long period of slow upheaval of these "horsten". So in proportion to their age so they occur at different levels, the oldest or first formed lying in the highest level, those which are younger gradually somewhat lower. These reefs therefore form together a slowly sloping more or less terraced covering or coating of coral-limestone. The entire thickness of this neogene formation from beyond the basins does not exceed 60 Meters.

Inside the "graben" where the neogene beds attain a much greater thickness, elements of terrigenous origin make their appearance in the upper portion of the Globigerina deposit and gradually it passes

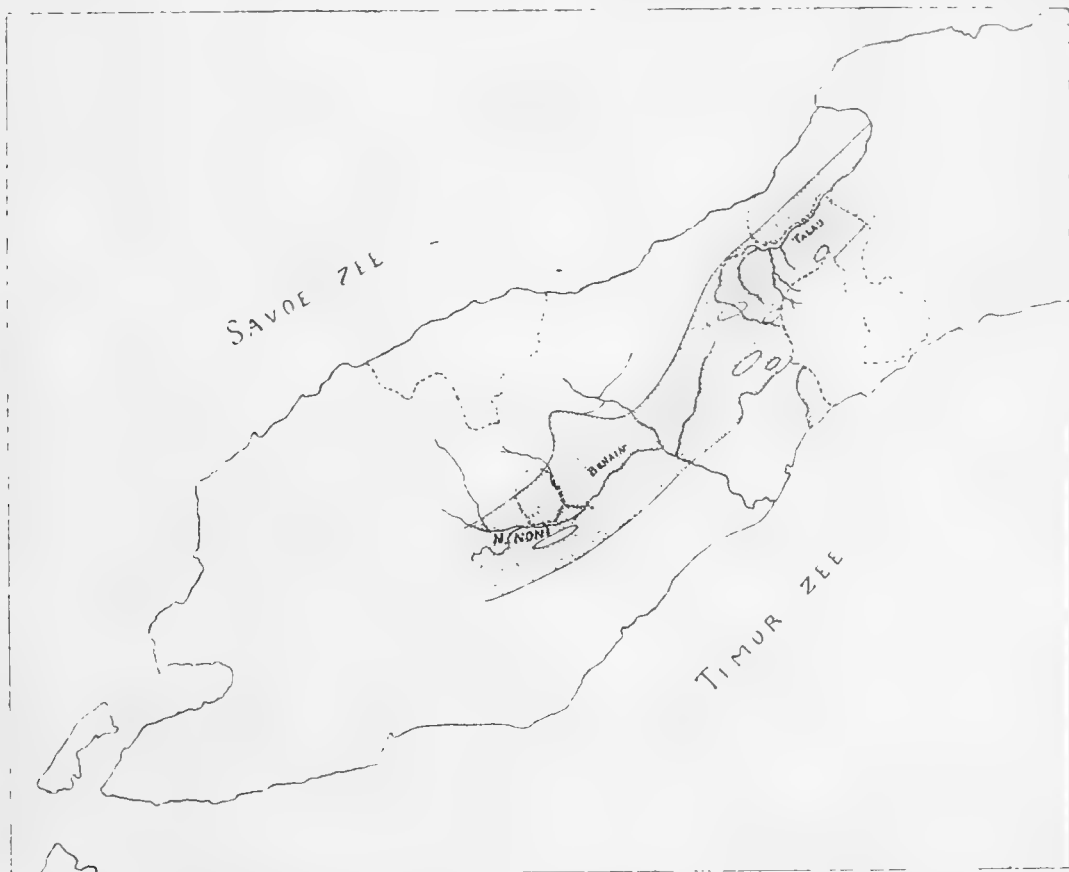


Fig. 1. Sketchmap showing the area covered by the later-tertiary deposits in Middle-Timor. Scale 1 : 2.560.000

it may be as well to explain that in case adjoining strips of land are affected by antagonistic movements and are separated one from the other by faults, the down-thrown strips or blocks are called "graben", whereas the upthrown strips or blocks are called "horsten".

into a sandy limestone, or even into a grit with calcareous cement. Thus the influence of land gradually increases and the higher strata consisting of marly claystones and marly sandstones are observed to contain numerous shells of the zone of shallow water which are regarded as of pliocene age<sup>1)</sup>

The above-mentioned basins or "graben" trend in a direction approximately parallel to the longitudinal axis of the island of Timor (fig. 1). In a portion of Middle-Timor, as e. g. between Kapan and Niki-Niki, one single undivided "graben" exists which might be termed the median neogene basin, although generally, the structure of the "graben" is more complicated being subdivided by ridges ("horsten") or islands of older formations, which are elongated as well in the direction of the longitudinal axis of the island. Thus in the eastern portion of Middle-Timor the later-tertiary basin is divided by the Mandeo-mountains into two troughs, the Talau-Insana-basin and the Benain-basin<sup>2)</sup>, while the latter more to the West again is subdivided by a narrow ridge of older formations into a northern Benain-Noilmoeti-basin and a southern Noil Lioe-basin. Faults of considerable character occur at the walls of the "graben", which by their influence have caused the younger tertiary strata in the basin to become suddenly curved and bent upwards near the edges. In many places a crush-breccia is found between the older formations and the tertiary strata thus indicating the position of these marginal or lateral faults.

During the formation of these "graben" by the slow subsidence of their deposits they remained always fairly well filled up with an accumulation of late tertiary sediments, from the character of which it may be gathered that the sea, although having occupied those basins, never attained a great depth.

These late-tertiary strata besides being tilted near the walls of the "graben", also show in places slight disturbances. The entire thickness of this formation in the "graben" is unknown although in my opinion in the Benain-basin it may safely be estimated at more than 500 metres.

True littoral formations such as conglomerates, oysterbanks, coral-reefs, etc. lie directly upon these pliocene deposits, and their thickness is at least 200 metres in the central axis of the larger or Benain-

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1) The pliocene age of these deposits is proved by MARTIN, who has examined the fauna of the marls of Fulumonu in the Talau-basin, which is identical with the fauna of the fossiliferous strata in the basin of the Benain. K. MARTIN. Tertiaer von Timor. Beiträge zur Geologie Ost-Asiens und Australiens. Serie I, Band III, p. 305. Leiden 1883—1887.

2) These two basins are united again West of the Mandeo-Mountains.

“graben”. One of the coralreefs in the Benain-basin (fig. 2) is of great thickness (70 Meters) and of considerable extension, being consequently an element of importance in the configuration of the land-

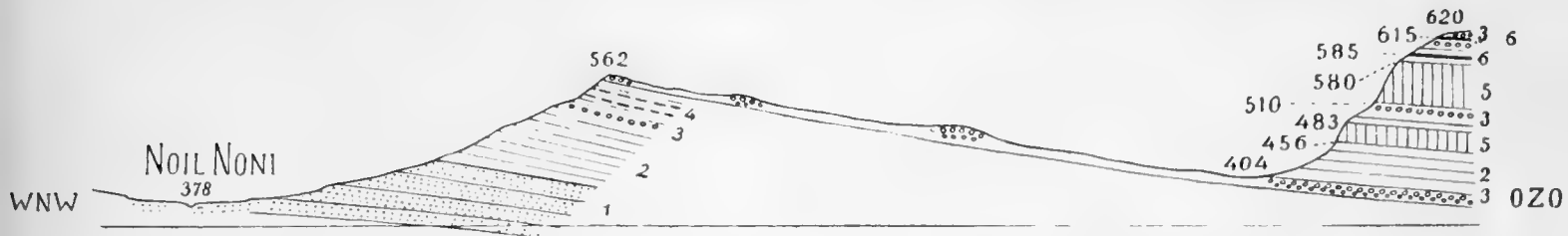


Fig. 2. Section across a portion of the Benain-basin in Middle-Timor.

1. Claystone and marl with shells, Pliocene.
2. Marls and sandy marls, containing in places marine organisms.
3. Conglomerate.
4. Sandy marl with *Placunna*.
5. Coralreefs, late-Pliocene or Pleistocene.
6. Oysterbanks.

Scale. 1 : 14.000.

Altitudes in Metres above sealevel.

scape ; on these coralreefs is again deposited a succession of layers of sandstone, conglomerates, oysterbanks, etc., all significant of a littoral origin. From their considerable thickness we must infer that these deposits were formed during a period of slow subsidence, which must have occurred at the end of the pliocene or at the beginning of the pleistocene age.

These reefs and other littoral deposits although getting thinner towards the edges (walls) of the basins, are not always confined to the “graben”, but in places they spread over a great area in Middle-Timor and overlap the older formations from which they are often separated by a well developed coarse basal conglomerate ; consequently they are also found resting unconformably upon the *Globigerina*-deposits where the latter are locally tilted at the edges of the “graben”. It is obvious that these coralreefs of late-pliocene or early-pleistocene age have been formed outside the “graben” in close proximity, although generally at a somewhat lower level, to the above-mentioned older reefs of probable miocene and pliocene age. It was not proved possible to discriminate in the field between these reefs of different ages, with certainty, but probably a future examination of the Foraminifera contained in them may lead to more accurate results.

In the “graben” there is no break in the succession or unconformity visible between the pliocene strata and the overlying reefs and

littoral deposits; and there can be no doubt that the last mentioned reefs both inside and outside the "graben" all belong to one and the same continuous formation, the connection of which has only been interrupted by later erosion.

During and just after the formation of these coralreefs a great portion of Middle-Timor must have been covered by a sea full of coral-islands and reefs. The higher mountain-groups (Moetis, Lakaän, Mandeo etc.) emerged as islands from this sea, and the conglomerates, formed simultaneously with and posterior to the coralreefs, prove that the islands must have been steep and high and that the running water must have transported a considerable amount of debris from them towards the surrounding sea.

It may be accepted that the majority of the big coralreefs were thus formed in late pliocene or early pleistocene times as they overlie and clearly therefore indicate a younger age than the marls with pliocene shells.

Further, *as these reefs were already formed*, a general upheaval of the island of Timor took place which possibly still continues. This upheaval, however, was not equally strong everywhere, consequently the elevated coralreefs are no longer found in a horizontal position but feebly sloping.

It appears that the upheaval of the central portion of the island has been from the beginning somewhat stronger than that of the southern and northern coastal regions.

In fact the reefs of the Diroen-ridge south of the Lakaän near the central axis of the island occur now at an altitude of 1283 Meters, about 680 Meters higher than those on the hills of the north coast at Babilo. The big reef also of the Gempol-cliff in the central portion of the island not far from Kapan has an altitude of 1250 Meters above sealevel, whereas in the southern mountainranges near Niki-Niki the highest altitude at which coralreefs are found is only 750 Meters.

Moreover, the upheaval of the land has been stronger at the edges of the basins ("graben") than in the basins themselves. Consequently the coralreefs which rest on the pliocene strata in the "graben" are no longer found in their original horizontal plane of deposition, but assume a feebly basin- or trough-shaped position and are besides split up into blocks of slightly different altitudes. It may be that this latter circumstance is caused by compression and the squeezing out of the soft and more or less plastic pliocene strata underlying the heavy compact coral limestones, although it might just as well be suggested that it is caused by a feeble continuation of the crustal

movements which had been present to account for the formation of the pliocene "graben" and "horsten".<sup>1)</sup>

During the prolonged period of recent upheaval the running waters were obliged to cut their courses with strong and increasing gradients. Narrow deep valleys, often true gullies (cañons) were formed which are characteristic of the topography of the greater part of the island. Numerous terraces are found along the courses of the rivers as well in connection with those rivers which have developed their systems within the late-tertiary basins, as also with those, where the systems lay entirely outside of the basins. This proves that the entire island of Timor took part in the recent upheaval, although not everywhere to the same extent.

This unequal or differential upheaval of the land has caused the rivers which flow within the tertiary basins to generally transverse, somewhere in their course, one or more of the strong layers of reef-limestone, at those places where those are comparatively little elevated. Thus the Benain has, in the central portion of the Benain-basin near the native village Nèke, at an altitude of 296 M. cut a narrow deep gorge of more than two miles in length through a thick stratum of coral limestone. In one portion of this gorge the running water undermined a portion of the coral limestone, and thus formed over the current, which is very deep and strong a natural arch or bridge which is now a much frequented road of communication.

<sup>1)</sup> My conclusions differ slightly from those of VERBEEK (R. D. M. VERBEEK, *Molukkenverslag. Geologische verkenningsstochten in het oostelijk gedeelte van den Ned. O.-I. Archipel. Jaarb. van het Mijneuzen XXXVII. Batavia 1908*). According to VERBEEK the coralreefs of the Talau-basin are of different age, and were all formed during the gradual upheaval of the land as fringing reefs, which are now found to be the older because of their higher level above the sea (l.c. p. 777).

The highest, those of the Diroen-ridge at an altitude of 1283 M. above sealevel, are regarded as of miocene age, those of Lahoeroes at an altitude of 569 M. of somewhat later date, and the lowermost, those of Fatoe Lamintoetoe at an altitude of 300 M. of pliocene age. These coralreefs diverge the older they are proportionally more from their original horizontal position; thus the oldest show a dip of 8°, those which are at a lower level of 5°40', whereas those which occur still further below dip only 3°50' (l. c. p. 357 and p. 778).

Although admitting that outside of the "graben", coralreefs of probably miocene age are found and that these ancient reefs occupy the highest levels now, I am of opinion that the majority of the elevated reefs i. e. the bulk of those which occur within the area of the "graben" including the Talau-basin, and also a part of those which are situated beyond the limits of the "graben", were formed before the commencement of the latest period of emergence (upheaval) of the island of Timor and consequently must be of the same late-pliocene or early-pleistocene age; and the above mentioned, feebly synclinal and somewhat disturbed and fractured position of the reefs, which spread continuously over large distances within the "graben", would be an explanation for the fact that these reefs are found at present in different altitudes, decreasing towards the central axes of the "graben".

In the same way the Talau-river just below its confluence with the Baukama at an altitude of 245 M. <sup>1)</sup> above sea-level, has cut a gorge which at present is 55 M. deep, across a high bank of coral limestone.

Theoretically one might expect, that during this prolonged period of upheaval, which possibly is still in progress, a series of fringing reefs had been formed all round the area of elevation. The current opinion is, of course, that the elevated coralreefs of Timor were formed in such a way from miocene times until now, during a continuous movement of upheaval of the land <sup>2)</sup>. The fact is, however, that not a trace of elevated fringing reefs is found along the north western and southeastern coast, where the island of Timor adjoins the eastern continuation of the deep depression of the Savoe-sea and the equally deep depression of the Timor-sea. The westernmost portion of the island, on the contrary, where it borders the shallow water which separates it from the island of Rotti, is covered with elevated fringing reefs.

If we look for an explanation of this remarkable fact, it is of importance to bear in mind that the island of Timor appears to be suddenly truncated and broken off by faults just along the north-western and southeastern coasts which border deep basins of the sea coming up close to the shore.

The late-tertiary or early-quaternary reefs and littoral deposits which form the uppermost portion of the neogene series of the Talau-basin, on the mountain-ridge of the northcoast for instance near Babilo, abruptly terminate with their full thickness in a steep cliff, facing the sea at an altitude of about 610 Meters. Evidently the strata once extended much further towards the North, but afterwards became detached. Between this point and the actual coast no trace of elevated coralreefs is found, whereas at the beach in the surf small reefs of living corals are abundant. This circumstance as well as the fact that along the north coast the hills rise with an uncommonly steep slope from the sea, tends to prove that the island of Timor is broken off towards the North. More convincing evidence still, is afforded by the south coast, where in the district of Amanatan the parallel ridges of the Amanoeban-mountainchain, which is mainly composed of Jurassic strata striking 010N-W10S (a direction differing about 12° from the general trend of the coast line), follow each other abruptly abutting against the coast and terminating in high cliffs.

<sup>1)</sup> VERBEEK, in his description of the tertiary basin of the Talau-river, also mentions this gorge l. c. p. 348.

<sup>2)</sup> R. D. M. VERBEEK, l. c. p. 777.

The sea deepens suddenly all along this coast and no trace of islands or shoals are found which might be regarded as the submarine continuation of those ridges. All observations made along this coast give support to the opinion that the island terminates here against a fault facing the Timor-sea.

I think it quite possible that the faults which thus terminate the island of Timor both towards the North and the South have been the cause of the absence of elevated reefs along those coasts of upheaval.

If we accept the existence of these breaks, the question arises: What has been detached towards the North and the South? Clearly it must be the sunken blocks of land which are found in the deep basins of the Timor-sea and the Savoe-sea.

To the North of the island of Timor the eastern continuation of the Savoe-sea has a depth of 3255 M. near the island of Kambing; to the South the depth of the Timor-sea is 3109 M. and this considerable depth is found much nearer to the coast of Timor than to the Sahul-bank which forms part of the continent of Australia.

Not only Timor, however, is thus bordered at both sides by deep sea-basins, but it is a coincidence which holds good for the majority, if not for all of the islands of the eastern portion of the archipelago, consequently, the origin of the deep sea-basins and the elevation of the islands in the eastern portion of the archipelago may be regarded as a simultaneous process between which a genetic connection must have existed.

The genesis of adjoining sunken and tilted blocks must be the result of one and the same crustal movement, which in my opinion would be the cause of a process of folding at great depths.

If the question were raised as to what might be seen at the earth's surface if an area were folded by crustal movement at a certain depth, I should be inclined to reply that its appearance would be similar to what obtains at present in the eastern portion of the Indian archipelago<sup>1</sup>). It is a well known fact that the folding of rock-strata is only possible under high pressure; it may therefore be inferred that folding can only originate at certain depths below the earth's surface. At the surface, in the zone of fracture, where the rocks cannot be plicated, the phenomena of deeply seated thrust and folding would be indicated by the presence of "graben" and "horsten", the former corresponding to the troughs, the latter to the saddles of the deeply seated folds. Generally speaking every range of tilted

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<sup>1</sup>) ABENDANON has arrived at a somewhat similar conclusion, in his analysis of the topography of the island of Celebes. E. G. ABENDANON, Celebes en Halmaheira, Tijds. K. Ned. Aandr. Genootsch. 2, XXVII. p. 1149, Leiden 1910.

blocks, or islands in our case, as well as every range of sunken blocks, or deep sea basins in our case, must indicate the position and the trend of the major folds, which are in mode of formation at a certain depth; thus the character of the deeply seated folds would be found reflected in the surface topography.

But then one has to take into account also, the submarine topography <sup>1)</sup> and fortunately the excellent deep sea chart of the Siboga-expedition enables us to do this <sup>2)</sup>.

The most salient feature on this map is the striking difference which exists between the western portion (the Java-sea and its surroundings), and the eastern portion (the Molucca-sea). The latter exhibits a complicated topography and great variations both in the depth of the sea and in the heights of the numerous islands, which generally emerge boldly from the sea; whereas the western area shows a slight and very uniform depth of the sea and smooth outlines of land which rises with a very gentle slope from the coast <sup>3)</sup>.

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<sup>1)</sup> In my opinion it is imperative to study the submarine topography, because the part of the surface of the earth hidden beneath the sea in this archipelago is so much greater than that of the islands. This itself is a favourable circumstance, because it tends to prove, that the basins until now were comparatively little filled up by products of erosion brought from the land, and consequently the surface topography originated by the recent crustal movements has been fairly well preserved at the bottom of the sea. The upraised islands of course are smaller and less high now than they would have been, were it not that the erosion had from the start counteracted the results of the upheaval. In or near large continents the chances for the preservation of a salient topography are much smaller, because the original features would have been much sooner obliterated by the effects of erosion and sedimentation. Thus in a portion of Northern Germany and the Netherlands, geologically not long since, crustal movements formed a surface topography, certainly not less complicated than that of the East-Indian archipelago, in which the levelling processes have been so powerful, that its original topographical details has become obliterated, with the result that at present only a trace of them can be seen at the surface; indeed we have to imagine the quaternary and a portion of the tertiary deposits removed to be able to realize the complexity of this topography.

<sup>2)</sup> G. A. F. TYDEMAN. Hydrographic results of the Siboga-expedition. Chart 1. Part III of M. WEBER. Siboga-Expeditie. Leiden 1903.

Soundings which have been made in the archipelago since the results of the Siboga-expedition were published, have proved, that the submarine topography is still more complicated than that shown on the chart. Very probably, the most important result of the researches of the Siboga-expedition i. e. the existence of a strikingly complicated submarine topography in the eastern parts of the East-Indian archipelago, will be more accentuated by future researches.

<sup>3)</sup> VERBEEK has already drawn attention to this striking difference between the western and the eastern portion of the archipelago and he pleads a causal origination for the presence of the deep sea-basins and the islands with elevated



This western portion with the tranquil topography both of the land and the sea-bottom, has not taken part in the more recent crustal movements; since the upheaval which raised the miocene sandstone formation in Central-Borneo to a level of more than 1000 M. above the sea, no movements of the soil have been recorded there, probably with the exception of the area immediately bordering the Street of Macassar. In the eastern portion of the archipelago, where a complicated topography of the land and the sea bottom prevails, deep sea-basins have been formed by subsidence; and, during the same time, ranges of islands have been elevated above the sea, caused by antagonistic movements which are probably still in course of progress. *It thus appears that in the latest geological period the crustal movements, in the geosynclinal or movable area between the Australian and the Asiatic continent, have been confined to the portion, immediately adjoining the Australian continent, i. e. between Borneo and Australia.*

In tropical regions generally, a coating of coral-limestone is formed along an elevated coast, as long as there are no causes to counteract or annihilate the results of the growth of successive fringing reefs during the period of upheaval.

This easily recognisable coating of coral-limestone (series of fringing reefs in different levels one above the other) in tropical regions, affords an excellent criterion from which may be judged whether a coast has been elevated in proportion to the level of the sea.

Now in the entire western portion of the archipelago with its undisturbed topography i. e. the land surrounding the Java-sea where, according to my opinion, no movements of the land in relation to the level of the sea have taken place in the latest geological time, raised coralreefs have not been recorded<sup>1)</sup>.

In the eastern portion of the archipelago with its complicated topography, where crustal movements have occurred, elevated coralreefs are found on the great majority of the islands.

*I believe, that generally speaking it may be accepted, that where coralreefs* (l.c. p. 817). VERBEEK, however, believes in an indirect cause for such a phenomenon. In his opinion the upheaval of the islands took place only after the deep sea-basins had already been formed, by the subsidence of landmasses; pressure exercised by the sunken blocks caused later folding at a great depth, as well as the upheaval of the islands (l.c. p. 816). In my opinion, however, the causal origin was of a direct nature; the subsidence of the deep sea-basins and the elevation of the islands took place at the same time, and both antagonistic movements were the results of one and the same phenomenon of thrust and folding at a certain depth.

<sup>1)</sup> Java, especially the southern coast, would have been subjected again to the crustal movements, which had occurred at the border between the Indian Ocean and the East-Indian archipelago.

*a deep sea chart shows a complicated topography the adjoining coasts must show signs of upheaval (in tropical regions, as a rule, elevated coralreefs), and where this is not the case one must expect no evidence of importance in favour of the upheaval of the adjoining coasts.*

If my suggestion is correct that folding at a certain depth is the cause of the simultaneous origin of both deep sea-basins and the elevation of the islands, the following phenomena would result:

1. The elevated islands would be grouped in rows, for they are nothing but the elevated though fractured strips of land on top of the saddles of the deeply seated folds. The trend of the rows of islands would indicate the line of strike of such folds, examples of which may be seen in the rows at Soemba-Timor-Timorlaut-Kei-Ceram-Buru; as also at Soembawa-Flores-Wetter etc.

2. The deep sea-basins would be elongated in one direction more or less exactly parallel to the adjoining rows of islands, because they are formed on top of the troughs of the deeply seated folds. For example I may quote the case of the Savoe-sea, the depth near the island Kambing, the Timor-sea, the Weber-depth, etc.

3. Near the surface, in the zone of fracture, one would also expect to find faults, which had broken the connection in the sides of the folds. Such faults would exist between the deep sea-basins and the elevated islands; and where the faults had repeatedly cut away the land at the coast, the development of elevated fringing coralreefs would have been hampered. This has taken place both at the north and the south coast of the island of Timor, and also at the islands of Moa and Leti.

4. All the islands of one row would be elevated, but the upheaval would have been very unequal, as can be observed if the islands are compared one with the other, or if an examination be made of different portions of one island. This is indeed the case in all the elevated islands, as can be principally deduced from the descriptions in VERBEEK'S Molukken-verslag.

5. There is no reason why faults should occur between adjoining islands belonging to one and the same elevated range (saddle of a deeply seated fold), which would hamper the development of elevated coralreefs. It is possible that this circumstance might explain why, at the western extremity of Timor, elevated fringing coralreefs appear to be so well developed.

6. Where the deeply seated fold, shows sudden bends or curves,

or where two systems of folds interfere<sup>1)</sup> exceptions to the above mentioned rules and complicated cases may be expected. The deep sea chart of the Siboga shows good examples of this fact.

**Zoology.** — “*On the Freshwater Fishes of Timor and Babber.*” By  
MAX WEBER and L. F. DE BEAUFORT.

The Timor Expedition, under leadership of Prof. G. A. F. MOLENGRAAFF, returned to Holland with extraordinarily rich mineralogical, palaeontological and geological collections and its leader has already communicated some important preliminary results, which are of great importance, not only to our knowledge of Timor, but also to the geological history of the whole indo australian archipelago. As they throw new light on the youngest phases in the development of the archipelago, they are of special importance to the zoogeographer too.

Therefore it is a memorable fact, that Prof. MOLENGRAAFF consented to our request to make a collection of freshwater fishes, when time and circumstances permitted, as thus important light is thrown on at any rate the younger phases of the evolution of the indo-australian archipelago.

We are glad to seize this opportunity to thank him as well as his collaborator Mr. F. A. H. WECKHERLIN DE MAREZ OYENS for the collection of well preserved specimens of fish, brought together by the lastnamed in different rivers of Timor and the island of Babber.

As far as we know, Babber was — ichthyologically — a terra incognita. The following fishes were collected by Mr. WECKHERLIN DE MAREZ OYENS in the rivers (Jer), which are mentioned next to the name of the fishes.

*Anguilla mauritiana* BENN. Jer Lawi, 7 Km. above mouth. Jer Toilila near Tepa, 500 M. above mouth.

*Caranx caranqus* BL. Jer Lawi, 7 Km. above mouth.

*Gymnapistus niger* C. V. Jer Lawi, 7 Km. above mouth.

*Eleotris gyrinoides* BLKR. Jer Toilila near Tepa, 500 M. above mouth. Jer Lawi, 7 Km. above mouth.

<sup>1)</sup> The East-Indian archipelago is situated in the area of junction of two systems of folding of the earth's crust, the alpine and circumpacific system, vide E. HAUG. Les géosynclinaux et les aires continentales. Bull. de la Soc. Géol. de France. 1900. 3. Sér. Vol. 28 p. 635. Whereas E. HAUG refers in this area to an “embranchement” of the two systems, SARASIN goes further and speaks of an actual conflict: “Ich habe noch immer den Eindruck, dasz es sich im malayischen Archipel um einen Konflikt zwischen den Kettensystemen der Tethys und denen der pazifischen Umrahmung handle”. P. SARASIN. Zur Tektonik von Celebes. Monatsberichte der deutschen Geol. Ges. 1912. p. 215.

*Eleotris (Culius) fusca* BL. Jer Toilila near Tapa, 500 M. above mouth.

*Eleotris (Belobranchus) belobranchus* C. V. Jer Lawi, 7 Km. above mouth.

*Gobius spec.* Jer Toilila near Tapa 500 M. above mouth.

*Sicyopterus micrurus* BLKR. Jer Lawi, 7 Km. above mouth. Jer Toilila near Tapa, 500 M. above mouth.

*Sicyopterus cynocephalus* C. V. Jer Lawi 7 Km. above mouth.

On the fishfauna of Timor BLEEKER<sup>1)</sup> wrote 7 papers between the years 1852 and 1863. There is not much to be learned from them for our purpose, however. Any exact account of the localities where they were taken, is lacking. Doubtless by far the greater part was captured in the litoral waters of Kupang and Atapupu. The following 7 only are specially recorded from a river near Deli:

*Megalops indicus* C. V. = *Megalops cyprinoides* BROUSS.

*Anguilla australis* RICHARDS.

*Atherina lacunosa* FORST. = *Atherina Forskali* RÜPP.

*Mugil brachysoma* C. V. = *Mugil sundanensis* BLKR.

*Acanthurus matoides* C. V.

*Caranx forsteri* C. V.

*Eleotris Hoedti* BLKR.

The locality and the nature of the fishes make it probable, that they were caught not far from the mouth of the river.

In 1894 the first named of us<sup>2)</sup> published a more extensive list of the fishes of Timor, chiefly due to Prof. A. WICHMANN, who was kind enough, during his stay in Timor in the spring of 1889, to collect the following fishes in the river Koinino and other small streamlets in the neighbourhood of Kupang, as well as in the river near Atapupu.

*Mugil (Blekeri* GTHR.?) river Koinino.

*Kuhlia marginata* C. V. river Koinino.

*Ambassis buroensis* BLKR. river near Kupang.

*Ambassis batjanensis* BLKR. river Koinino.

*Therapon jarbua* FORSK. river near Kupang.

*Caranx hippos* L. river near Kupang.

*Eleotris hoedti* BLKR. river near Atapupu.

*Eleotris fusca* BL. SCHN. river near Atapupu.

*Gobius celebius* C. V. rivers near Kupang.

*Gobius melanocephalus* BLKR. river Koinino.

*Sicyopterus Wichmanni* M. WEB. near Kupang.

1) Nat. Tijdschr. Ned. Indië III, 1852. p. 159—174. Ibid. VI, 1854. p. 203—214. Ibid. XIII, 1857. p. 387—390. Ibid. XVII, 1858 p. 129—140. Ibid. XX, 1859. p. 442—445. Ibid. XXII, 1861, p. 247—261. Ned. Tijdschr. Dierk. I, 1863, p. 262—276.

2) MAX WEBER. Zool. Ergebnisse einer Reise in Niederl.-Indiën. III, 1894. p. 438.

Then Dr. H. TEN KATE collected a few freshwater fishes, which have been published by Dr. C. L. REUVENS<sup>1)</sup>. These are:

*Anguilla bengalensis* (Gray) Gthr. = *Anguilla mauritiana* Benn. from a lake near Baun.

*Anabas scandens* Dald. near Amarassi and from lake Nefko near Oikaliti.

Lastly Mr. H. A. LORENTZ was kind enough to collect in August 1909, when passing Kupang on his way to New Guinea, the following fishes from the river Koinino:

*Eleotris (Belobranchus) belobranchus* C. V.

*Gobius celebius* C. V.

*Gobius melanocephalus* BLKR.

The great value of the fishmaterial collected by the Timor expedition lies in the fact, that it comes from the interior of Timor, far away from the sea, and from altitudes varying between 200 and 900 M. It gives a picture of the fishfauna in the upper course of the rivers, while the previously known material came from the lower course of the rivers. The collection consists of the species mentioned below, from the following localities:

1. Mota Berluli, District Djenilu, Belu, 1 Km. above mouth.

2. Noil Enfut (= Noil Mauden) between Wikmurak and Oi Lollo, District Insana, area of the river Noil Benain, about 200 M. above sea.

3. Area of the river Mota Talau, from streamlet without name near camp Naitimu, Belu, about 250 M. above sea.

4. Noil Bidjeli (= Noil Noni), near camp Bidjeli, upper area of the river of Noil Benain, District Mollo, about 350 M. above sea.

5. Noil Aplaal (= Noil Besi), near camp Aplaal, District Miomaffo, about 500 M. above sea.

6. Noil Besi near path from Fatu Seinaan to Bonleo, about 900 M. above sea.

7. River Bele, near the source of the river Noil Tuke, District Amanzebang, about 700 M. above sea.

*Anguilla mauritiana* BENN., Noil Besi, River Bele.

*Anguilla celebesensis* KAUP, River Bele.

*Aplocheilus celebensis* M. WEB., Area of the river Mota Talau.

*Mugil spec.* Mota Berluli.

*Aeschrichthys Goldiei* MACLEAY, Noil Bidjeli.

*Kuhlia marginata* C. V., Noil Bidjeli, Noil Aplaal.

<sup>1)</sup> C. L. REUVENS. Fresh and brackish water fishes from Sumba, Flores, Groot-Bastaard, Timor, Samaoe and Rotti. Notes Leyden Museum XVI 1895, p. 154.

	In Timor.		Also recorded from sea?	Distribution outside Timor.
	Mouth of rivers (brackish)	Fresh- water		
Megalops cyprinoides Brouss.	+	-	yes	Indopacific.
Anguilla celebesensis Kaup	-	+	} Katadrom fishes.	Eastern part of indo- australian Archipelago to Westpacific islands.
Anguilla mauritiana Benn.	-	+		From East Africa to Westpacific islands.
Anguilla australis Richards.	+	-		From India to Australia and New-Zeeland.
Aplocheilus celebensis M. Web.	-	+	no	Celebes.
Atherina Forskali Rüpp.	+	-	yes	From Red Sea to West- pacific islands.
Mugil spec. juv.	-	+	-	-
Mugil (Bleekeri Gthr.?).	-	+	brackish water	Banka, Aru-islands.
Mugil sundanensis Bleeker	+	-	yes	Indo-australian Archi- pelago.
Aeschrithys Goldiei Macleay	-	+	no	South New Guinea, Philippines.
Anabas scandens Dald.	-	+	no	From Ceylon through indo-australian Archipel. to Halmahera and Batjan?
Kuhlia rupestris C.V.	+	+	no	From East Africa to Westpacific islands.
Kuhlia marginata C.V.	-	+	yes	Indo-australian Archipel. to Westpacific islands.
Toxotes jaculator Pall.	+	-	no	Indo-australian Archipel.
Ambassis buroensis Bleeker	-	+	yes	Indo-australian Archipel.
Ambassis batjanensis Bleeker	-	+	yes	Indo-australian Archipel.
Lutjanus fuscescens C.V.	-	+	brackish water	Indo-australian Archi- pelago to Westpacific islands and China.
Therapon jarbua Forsk.	-	+	yes	Indo-pacific.
Therapon cancellatus C.V.	-	+	yes	Indo-australian Archipel.
Acanthurus matoides C.V.	+	-	yes	Indo-pacific.
Caranx forsteri C.V.	+	-	yes	Indo-pacific.
Eleotris Hoedti Bleeker	+	+	brackish water	Brackish and freshwater from India to Westpacific.
Eleotris belobranchnus C.V.	-	+	brackish water	Brackish and freshwater of Indo-australian Archip.
Eleotris fusca Bl. Schn.	-	+	brackish water	Brackish and freshwater of Indopacific.
Eleotris gyrinoides Bleeker	-	+	brackish water	Brackish and freshwater of Sumatra and Celebes.
Gobius celebius C.V.	-	+	yes	Seas and rivers of Indo- australian archipelago.
Gobius melanocephalus Bleeker	-	+	yes	Seas and rivers of India and Indo-australian Archi- pelago.
Sicyopterus Wichmanni M. Web.	-	+	no	Flores.
Sicyopterus cynocephalus C.V.	-	+	no	Indo-Australian Archipel.

*Kuhlia rupestris* LACÉP., Noil Aplaal.

*Lutjanus fuscescens* C. V., Mota Berluli.

*Therapon cancellatus* C. V., Noil Aplaal.

*Eleotris (Ophiocara) Hoedti* BLKR., Mota Berluli.

*Eleotris gyrioides* BLKR., Mota Berluli, Noil Enfut.

*Gobius celebius* C. V., Mota Berluli.

*Gobius melanocephalus* BLKR., Mota Berluli, Noil Enfut.

*Sicyopterus cynocephalus* C. V. Noil Enfut, Noil Besi.

The zoogeographical importance of all the species hitherto known from the freshwater of Timor will be more pronounced in a table in which is mentioned at the same time whether the species are known to inhabit the sea, in which case it is proved that salt water does not constitute a barrier against their distribution. Furthermore the distribution of the mentioned species is noted in our table.

From this table the following may be deduced:

1. Contrary to expectation Timor misses every australian or papuan element in its freshwater fishfauna. We mean by that the *Melanotaeniidae*, which are only known from Australia, New Guinea, Waigeu and the Aru islands and which are still represented on lastnamed islands by *Pseudomugil* and *Rhombatractus*, and further such forms as *Neosilurus*, *Eleotris aruensis* M. WEB., *E. Mertoni* M. WEB., *E. mogurnda* RICHARDS, which are also found on the Aru islands.

2. On the other hand a few fishes: *Anabas scandens* DALD. and *Aplocheilus celebensis* M. WEB., occurring in the freshwater fauna of Timor, are forms which are entirely lacking in the freshwater of the australian or papuan region.

3. The most striking fact however is, that 15 of the 28 enumerated species occur as well in the sea, temporarily (*Anguillidae*) or permanently, and 6 of them also in brackish water. The 7 remaining are hitherto only known from freshwater. From these 7 *Aeschrichthys Goldiei* MACL., *Kuhlia rupestris* C. V., *Sicyopterus Wichmanni* M. WEB. and *Sicyopterus cynocephalus* C. V. are closely related to forms for which salt water, or at least brackish water does not form a hindrance in their dispersion.

In other words the freshwater fishfauna of Timor has a marine character, it is almost totally composed of immigrants from the sea.

This very remarkable phenomenon can be explained by what the geological history of Timor teaches, as conceived by MOLENGRAAFF. To us the following is of importance.

Timor was covered by sea during a very great part of the pleistocene. The high mountains however (Mutis, Lakaan etc.) projected above the sea. They must have been comparatively high at that time

too, as the water, running in torrents from their sides, carried down much gravel. It was evidently a landformation not very apt to lodge a freshwater fauna of any importance. It is difficult to ascertain whether elements of this fauna still survive in the present fauna. This might possibly be the case with *Aplocheilus celebensis* M. WEB. and *Anabas scandens* DALD., which form a special element in the present fauna. One of these, *Aplocheilus* belongs to the family *Poeciliidae*, several genera of which are known from the early tertiary; and *Anabas scandens* has a very wide range of distribution, from the continent of Asia to the eastern part of the indo australian archipelago.

The recent fishfauna only came to full development when Timor was raised to its present level in post pleistocene times. This very young land developed a system of rivers, which could only be populated by such fishes, as are not hindered by salt water in their distribution. Timor, when rising, was surrounded by sea. The ichthyological material tends to prove that this was originally a shallow sea, possibly surrounding other greater or smaller islands in the neighbourhood, as, for several elements of the freshwaterfauna of Timor, a deep sea with a high salinity would form an unsurmountable barrier. Such a sea could only have been formed after the immigration in the freshwater was accomplished for the greater part.

We are of opinion that this is in accordance with the views of MOLENGRAAFF, who thinks that the formation of the deep seas along the north and south coast of Timor took place in connection with the final upheaval of the island, and that this has been the latest event.

**Physics.** — “*On the Deduction of the Equation of State from BOLTZMANN’s Entropy Principle.*” By Dr. W. H. KEESOM. Supplement No. 24a to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of April 26, 1912).

§1. *Introduction.* Since the two great advances made by VAN DER WAALS in deducing his equation and in developing the theory of corresponding states therefrom, the theoretical investigation of the equation of state for a single component substance has been developed in various directions, particularly by VAN DER WAALS himself; these developments have cleared up and enriched our knowledge of various circumstances which influence the equation of state, and which had



been left out of account in the first deduction of the equation. For example, we may refer in particular to the recent researches of VAN DER WAALS on the influence of apparent association. On the other hand, there has been collected much valuable experimental material, which has already, on various occasions, been compared with the results obtained from theoretical assumptions. In the meantime, while these researches are being continued, it seems desirable and opportune to undertake a systematic investigation of the equation of state over a region in which not only reliable experimental data can be obtained, and are in fact already accessible in part, but which also permits of a rigorous theoretical investigation.

KAMERLINGH ONNES <sup>1)</sup> has started to systematically collect, arrange and incorporate into his empirical equation the experimental results already accessible over the whole region which has been already investigated for the equation of state. Amongst other effects of this empirical equation is that it makes it easy to compare different substances from the point of view of the principle of similarity, and in this respect it has already led to a number of valuable conclusions. For a general review of these conclusions we may refer to an article on the equation of state which is to appear in the *Encyklopädie der Mathematischen Wissenschaften* and is now passing through the press; we shall refer to this paper as *Suppl. N<sup>o</sup>. 23*.

In investigating the most suitable expression for the equation of state preference was finally given (cf. *Comm. N<sup>o</sup>. 71 § 3*) to a series of increasing powers of  $v^{-1}$  (omitting the odd powers above 2 and closing the series with  $v^{-8}$ ). With a small deviation from the notations of *Comms. N<sup>o</sup>. 71 and 74* we may write the equation in the form

$$pv = A \left\{ 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} + \frac{E}{v^6} + \frac{F}{v^8} \right\} \dots \dots \dots (1)$$

(cf. *Suppl. N<sup>o</sup>. 23*).

The form of this equation shows that, from an experimental point of view, the method most immediately indicated for proceeding to obtain correspondence between theory and experiment is to successively determining, both theoretically and experimentally, the various virial-coefficients  $A, B, C$  etc., over a temperature region as extensive as possible for substances for which one would expect it necessary to make the least complicated assumptions regarding molecular structure

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<sup>1)</sup> H. KAMERLINGH ONNES, *Comm. No. 71* (June 1901), *No. 74*, *Arch. Néerl.* (2) 6 (1901), p. 874.

and molecular action. This is especially the case with the first coefficients  $A$ ,  $B$  and  $C$ , as their values can be experimentally obtained with pretty high accuracy quite independently of any special assumptions which may be made regarding subsequent terms; while, from the theoretical point of view, the means are at hand for deducing these virial-coefficients from various special assumptions regarding the structure and action of the molecules<sup>1)</sup>.

With regard to the first virial-coefficient  $A$  we may remark that one may write

$$A = RT \quad . . . . . (2)$$

( $R$  is the gas constant,  $T$  the temperature on the KELVIN scale) for non-associative substances over the whole temperature region hitherto investigated. With regard to the question as to whether such substances would exhibit another law of dependence upon temperature in another region (e.g. at the lowest possible temperatures) we may refer the reader to Suppl. N<sup>o</sup>. 23.

Both the present and the following paper aim at making a beginning with the deduction of the second virial-coefficient,  $B$ , from certain special assumptions, having in view its completion in subsequent papers by a comparison with results obtained from experiment.

In his *Elementary Principles in Statistical Mechanics* GIBBS developed methods which in principle enable us to deal with any molecular-kinetic problem concerning the equation of state, as long as we limit ourselves by the assumption that the mutual actions of the molecules conform to the HAMILTONIAN equations. ORNSTEIN<sup>2)</sup> adapted this method to the deduction of the equation of state and applied it. In Suppl. N<sup>o</sup>. 23 the method indicated by BOLTZMANN in his *Gastheorie* II § 61 and based immediately upon the BOLTZMANN entropy principle is developed in general terms. This method, too, seems suitable for the solution of all problems concerning the equation of state of systems in which the mutual actions of the molecules conform to the HAMILTONIAN equations. It has been shown by LORENTZ<sup>3)</sup>

<sup>1)</sup> In this connection it must be remembered that, as noticed in § 1 of Comm. No. 74, the virial-coefficients in the polynomial (1) differ from those of the corresponding infinite series in which all the positive powers of  $v^{-1}$  are present. The more attention must be paid to this point, the higher the coefficients concerned; it will be quite appreciable with  $C$  on account of the absence of the  $v^{-3}$  term in (1), while  $D$  in (1) can no longer be regarded as approximating to the coefficient of  $v^{-4}$  in the infinite series (cf. Comm. N<sup>o</sup>. 74 § 1).

<sup>2)</sup> L. S. ORNSTEIN. Diss. Leiden 1908.

<sup>3)</sup> H. A. LORENTZ. Physik. Z. S. 11 (1910), p. 1257.

that it leads to the same results as the GIBBS method of the canonical ensemble. Although the two methods can therefore be regarded in principle as equivalent, the BOLTZMANN method seems to possess certain advantages over the other, e.g. its terminology can be more directly applied to the physical conception. <sup>1)</sup>

As Suppl. N<sup>o</sup>. 23 is not yet published we may here give a short general account of this method, which forms the basis of the subsequent developments.

§ 2. *General formulation of the method of obtaining the equation of state of a single component substance from the BOLTZMANN entropy principle.* In the general formulation of the method we shall follow BOLTZMANN, *Gastheorie* II. § 36, and determine the momentary state (PLANCK's micro-state <sup>2)</sup>) of a system of molecules whose motions, under the influence of their mutual forces, can be regarded as determined by HAMILTON's equations <sup>3)</sup> in terms of a finite number of generalised coordinates and the corresponding momenta for each molecule. We shall define a *micro-complexion* <sup>4)</sup> as a state in which, for instance, the coordinates  $q_1 \dots q_s$  and the momenta  $p_1 \dots p_s$  of the first molecule lie between the limits  $q_{1i}$  and  $q_{1i} + dq_{1i}$ ,  $q_{2i}$  and  $q_{2i} + dq_{2i} \dots q_{si}$  and  $q_{si} + dq_{si}$ ,  $p_{1i}$  and  $p_{1i} + dp_{1i}$ ,  $p_{2i}$  and  $p_{2i} + dp_{2i} \dots p_{si}$  and  $p_{si} + dp_{si}$ , those of the second molecule between  $q_{1j}$  and  $q_{1j} + dq_{1j}$  etc.

In this, the micro-differentials <sup>5)</sup>  $dq_{1i}$  etc. must so be chosen that the specified distribution of molecules according to generalised coordinates and momenta is sufficient to fix the energy of each molecule in the micro-complexion as lying between definite limits which, in the problem under consideration, may be regarded as coincident, and also to enable one to ascertain if possible special conditions (e.g. mutual impenetrability, in the case of molecules supposed rigid) have been fulfilled. We assume that  $dq_{11} = \dots = dq_{1i} = dq_{1j} = \dots dq_{1s}$ ,  $dq_{21} = \dots$ ,  $dp_{11} = \dots dp_{1i} = dp_{1j} = dp_{1s}$  etc. or, at least, that the

<sup>1)</sup> And also in this that by this method the most probable distribution of molecules according to definite coordinates or momenta is at the same time determined, and also an expression is found for the BOLTZMANN *H*-function for the particular case under consideration.

<sup>2)</sup> M. PLANCK. Acht Vorlesungen p. 47 sqq

<sup>3)</sup> In the application to collisions between molecules which are regarded as rigid bodies we shall, if necessary, regard the collision as a continuous motion subject to very great accelerations.

<sup>4)</sup> Derived from BOLTZMANN's "Komplexion". Comp. L. BOLTZMANN. Wien Sitz.-Ber. 76 (1877), p. 373; Wiss. Abh. 2, p. 164.

<sup>5)</sup> M. PLANCK. Acht Vorlesungen, p. 59.

different elements of the  $2s$ -dimensional space involving the coordinates  $p$  and the momenta  $q$  (the micro-elements) are of the same size.

We consider now, in general, states of the system of molecules which are defined by certain conditions — formulated in detail for each special problem — in such a way that the number of molecules or of groups of molecules is determinate for which e.g. certain coordinates, mutual distances or orientations of the molecules, their momenta or their relative velocities lie between limits previously assigned. The formulation of these special conditions and the choice of limits must so be made that the supposed numbers of molecules etc., are sufficient to determine, in so far as the particular problem under discussion is concerned, the state of the system as seen by a macro-observer at the particular moment for which those numbers are given. In this we are in no case concerned with the individuality of the molecules (we assume throughout that we are dealing with a single component substance). The limits to which we referred must, moreover, be so chosen that the macro-state thus determined can be realised from a very large number of different micro-complexions. The assemblage of these micro-complexions we shall call a *group macro-complexion*<sup>1)</sup>.

As a foundation for further development we shall now assume that all micro-complexions represent cases of equal probability<sup>2)</sup>. From this it follows immediately that the *probability*,  $W$ , of the occurrence of any group macro-complexion is proportional to, or, if we care to neglect an arbitrary factor, is equal to the number of micro-complexions contained in the group macro-complexion<sup>3)</sup>.

In many cases it will facilitate the calculation of this number to first obtain the number of micro-complexions contained in an *individual*

<sup>1)</sup> For constructing a clear molecular kinetic interpretation of a definite macro-state, in particular regarding the number of the different micro-states by which it can be realised, we regard here as in the GIBBS method at any particular moment an assemblage (ensemble) of systems, independent of each other identical as regards number, structure and actions of their component particles and as regards their exterior coordinates, each of these systems forming a definite micro-complexion realising that macro-state. Cf. BOLTZMANN, *Wiss. Abh.* 1, p. 259; 3, p. 122; MAXWELL, *Scient. pap.* 2, p. 713. [Note added in the translation.]

<sup>2)</sup> In the present paper we shall not justify this assumption, which, in so far as it affects the choice of micro-elements, is founded upon LIOUVILLE's theorem, but for it we may refer to the writings of BOLTZMANN, PLANCK (e.g. *Acht Vorlesungen*, p. 56), and others. (Compare also Art. IV 32 by P. and T. EHRENFEST in the *Math. Encykl.*, particularly note 170).

<sup>3)</sup> In order to conform to the common definition of probability as a fraction between 0 and 1 in value we should have to divide by the assumed value of the constant total number of micro-complexions possible, which would have to include all possible values of energy and volume which occur in our considerations. This constant is of no importance in any of our considerations, so we shall omit it.

*macro-complexion*. The definition of the latter complexion follows from that of the group macro-complexion by taking account of the individuality of the molecules. The number of micro-complexions in the individual macro-complexion has to be separately determined for each special problem, and this, multiplied by the number of individual macro-complexions contained in the group macro-complexion gives the number of micro-complexions contained in the group macro-complexion. The number of individual macro-complexions contained in the group macro-complexion, which is readily obtained from the theory of permutations, we shall call the *permutability index* of the macro-complexion <sup>1)</sup>.

From the value thus obtained for the probability of a group macro-complexion one can ascertain which group macro-complexion is the most probable in a self-contained system of molecules of given energy and volume. According to BOLTZMANN the distribution of molecules according to the coordinates etc. determining it, obtained for this macro-complexion, corresponds macroscopically to a state of equilibrium of the system of molecules.

BOLTZMANN'S entropy principle can now be formulated in such a way that the entropies of different macroscopically determined states are, if we omit an arbitrary additive constant, proportional to the logarithms of the probabilities of the different group macro-complexions corresponding to those macro-states. In this it is understood that these macro-complexions are determined with the same limits (equal elements of corresponding spaces) for the coordinates etc.

In the simple case, in which the same number of micro-complexions is present in each of the individual macro-complexions, as in the deduction of the equation of state for molecules whose dimensions and mutual attractions are neglected <sup>2)</sup>, the entropy is then simply proportional to the permutability index of the macro-complexion.

In general we may write

$$S = k_P \log_e W. \quad \dots \dots \dots (3)$$

in which  $S$  represents the entropy, and  $k_P = R_M/N$  where  $R_M$  is the molecular gas constant and  $N$  is the AVOGADRO number (i. e. the number of molecules in the gram molecule). We then obtain for the entropy in the state of equilibrium of a gas whose molecules are regarded as having no dimensions and as exerting no mutually attractive forces, a function of volume and temperature which agrees with the thermodynamic expression for the entropy.

<sup>1)</sup> Differing slightly from L. BOLTZMANN, loc. cit. p. 243 note 4.

<sup>2)</sup> Comp. M. PLANCK, Wärmestrahlung, p. 140 sqq.; Acht Vorlesungen, Vierte Vorlesung.

If, by introducing special assumptions regarding the molecules and their mutual forces, one calculates, in the manner here indicated, the entropy  $S$  in the equilibrium condition for given energy  $U$  and volume  $V$ , one obtains directly a fundamental equation of state from which both the specific heats and the thermal equation of state can be deduced.

§ 3. *Deduction of the virial-coefficient  $B$  for rigid, smooth spheres of central symmetry and subject to VAN DER WAALS' forces of attraction.*

Although this problem has already been repeatedly treated, first by VAN DER WAALS himself in the deduction of his equation of state, and since then, in particular, by PLANCK<sup>1)</sup> by a method which is essentially the same as that here developed, we may yet utilise this simple case as an introduction to our treatment of the succeeding more complex cases. The description of these can then be shortened by referring to corresponding definitions and operations in the present problem.

Determination of the macro-complexion:

Two states which a macro-observer can distinguish as different may be regarded as having their differences arise from the presence in definite elements of volume of different numbers of molecules in the two cases, and also from different distributions of speed in those volume-elements. To determine a macro-complexion we therefore take the three-dimensional spaces which are available for each molecule with respect to its coordinates  $x, y, z$  and the velocities  $\xi, \eta, \zeta$  of its centre, and divide them up into equal elements ( $dx_1 dy_1 dz_1 \equiv$ )  $dv_1, dv_2 \dots dv_k$ , and ( $d\xi_1 d\eta_1 d\zeta_1 \equiv$ )  $dw_1, dw_2 \dots dw_l$ .

In this we make  $dv_1 \dots$  so great that each contains on the whole a great number of molecules, and yet sufficiently small for the density variations within those elements of volume to escape the notice of the macro-observer; the elements  $dw_1 \dots$  are also chosen so great that to each corresponds a large number of molecules in  $dv_1 \dots$  and yet so small that  $d\xi_1, d\eta_1, d\zeta_1 \dots$  are small in comparison with the mean speed.

The group macro-complexion is now determined by the conditions that

$$\begin{array}{l} n_{11} \text{ unspecified molecules "are present" in } dv_1 dw_1 \\ \vdots \\ n_{kl} \text{ ,, ,, ,, ,, ,, } dv_k dw_l . \end{array} \quad (4)$$

Determination of the micro-complexion:

As far as velocities<sup>2)</sup> are concerned, the micro-complexion can be

<sup>1)</sup> M. PLANCK, Berlin Sitz.-Ber. 32 (1908), p. 633.

<sup>2)</sup> As the velocities differ from the momenta only by a constant factor, we may

determined from the same elements of the proper space as the macro-complexion. With regard to the distribution of the molecules throughout the space we must distinguish between various elements of volume, which are supposed small in comparison with the dimensions of a molecule, for, in ascertaining if a certain micro-complexion occurs in the macro-complexion determined by (4), it is of importance to know if the centre of any particular molecule lies within or without the distance sphere of any other molecule. Hence we divide the volume-elements of the macro-complexion into smaller volume-elements, thus

$$\begin{array}{l} dv_1 \text{ into } \alpha \text{ equal volume-elements } d\omega_{11} \dots d\omega_{1\alpha} \\ dv_2 \text{ ,, ,, ,, ,, } d\omega_{21} \dots d\omega_{2\alpha} \\ \text{etc.} \end{array}$$

A micro-complexion is now determined by specifying for each molecule in which of the elements  $d\omega$  and  $dv$  it is present at the particular moment under consideration (understanding that a molecule is present in the micro-volume-element  $d\omega$ , when its centre of mass is there).

$W$  is now the number of micro-complexions thus determined present in the macro-complexion given by (4); in this we must remember that all micro-complexions are excluded in which the distance separating the centres of any two molecules is smaller than the diameter of a molecule.

For the permutability index of the macro-complexion we obtain

$$\frac{n!}{n_{11}! n_{12}! \dots n_{kl}!}$$

As we shall have to deal only with such macro-complexions as correspond to states of equilibrium or to states differing but little therefrom, it follows from the conditions laid down regarding the magnitude of  $dv$  and  $d\omega$ , that for each element  $dv_i d\omega_j$  of the 6-dimensional space in which, for any specified state, molecules may be present, the number  $n_{ij}$  will be large. We shall, in the meantime, be obliged to compare macro-complexions whose total volumes  $v$  are not the same<sup>1)</sup>, for instance in the development of the thermal equation of state. This can be done if, in the determination of the macro-complexion, we also take account of volume-elements lying in this case use equal elements in the velocity diagram for determining micro-complexions of equal probability.

<sup>1)</sup> When, as in the present instance, we consider states in which the substance is not split up into different phases, we shall indicate the volume etc. by small letters  $v, u, s$ , which, when referred to 1 gram of the substance, can then be regarded as specific quantities.

outside the volume  $v$ . A similar remark holds regarding the energy  $u$ . The conditions represented by (4) must then be so understood that the number of molecules in each of these outlying elements of the 6-dimensional space is zero, and for each of these elements the figure 1 must be put in the denominator of the permutability index.

We have still to calculate the number of micro-complexions contained in the individual macro-complexion; this is determined by specifying that

$$\begin{array}{l} n_{11} \text{ specified molecules are present in } dv_1 dw_1 \\ \vdots \\ n_{kl} \text{ ,, ,, ,, ,, ,, } dv_k dw_l. \end{array} \quad (5)$$

These micro-complexions differ only in the different dispositions of the  $n_1 = n_{11} + \dots + n_{kl}$  molecules in the volume-element  $dv_1$  etc. The different volume-elements are here to be regarded as independent of each other. We then obtain the total number of micro-complexions by calculating the number of different ways in which the  $n_1$  molecules can be placed in the volume  $dv_1$ , the same then for  $dv_2$  etc., and by then multiplying these numbers together.

Let us first put the first of the  $n_1$  molecules in  $dv_1$ . For this there are  $x$  places available. For the second molecule there are then left

$$x \left\{ 1 - \frac{\frac{4}{3}\pi\sigma^3}{dv_1} \right\} \text{ places available. Of these there is a comparatively small}$$

number for which the distance between the centres of molecules is such that the distance spheres of the two molecules partially overlap. In placing the third and succeeding molecules we shall omit these cases, for bringing them into the calculation would introduce terms of the second order of small quantities compared with the principal terms of  $W$ , and would have no effect upon the value of the virial-coefficient  $B$ . The influence of these terms would have to be more closely investigated only in the determination of  $C$  and succeeding coefficients. The number of places available for the third

$$\text{molecule can then be written } x \left\{ 1 - 2 \cdot \frac{\frac{4}{3}\pi\sigma^3}{dv_1} \right\}. \text{ Proceeding in this}$$

fashion we obtain

$$x^{n_1} \prod_{i=1}^{n_1-1} \left\{ 1 - i \frac{\frac{4}{3}\pi\sigma^3}{dv_1} \right\}$$

different dispositions of the  $n_1$  molecules in  $dv_1$ . Doing the same for  $dv_2$  etc., we obtain the number of micro-complexions in the individual macro-complexion.



After multiplying by the permutability index, a little reduction in which use is made of STIRLING'S formula, gives with sufficient approximation

$$\log_e W = - \sum_{dv} \sum_{dw} n_{11} \log_e n_{11} - \frac{4}{3} \frac{\pi \sigma^3}{dv_1} \sum_{dv} \frac{n_1^2}{2} \dots \dots \dots (6)$$

In this, terms have been omitted which remain constant when  $n$  is constant and the division into elements remains the same.  $\sum_{dv}$  and  $\sum_{dw}$  indicate summations taken over all the elements  $dv$  and  $dw$ . Use has also been made of the fact that the elements  $dv$  are all of the same size.

The expression which one obtains for BOLTZMANN'S  $H$ -function by reversing the sign of (6); agrees to the degree of approximation here given, with the expression given by ORNSTEIN<sup>1)</sup> for this case.

State of equilibrium:

This is determined by the condition that for constant  $v$  and  $u$ ,  $W$  is a maximum. The condition  $v = \text{const.}$  is fulfilled by varying only the values of  $n_{11}$ , etc. which occur in (6), and keeping  $n_{11} + \dots + n_{kl} = n$  constant. With regard to the condition  $u = \text{const.}$  the assumption that the molecules behave as if they were rigid *smooth* spheres, of central symmetry (so that their density is constant or only a function of the distance from the centre, and therefore their mass centres and their geometrical centres coincide) enables us to disregard angular speeds about axes through their mass centres. To enable us to find an expression for the potential energy we shall assume that the macro-volume-elements are great in comparison with the sphere of action of a molecule. With reference to the potential energy we shall, in conformity with the assumptions underlying the VAN DER WAALS attractive forces, further assume that, in states of equilibrium and in states closely approximating thereto, each sphere of action can be regarded as being uniformly filled with the number of molecules which that sphere would contain if the molecules were uniformly spread over the whole macro-volume element. In making this assumption cover even the molecules which lie near the boundaries of the volume-element we neglect the influence of capillary forces. Calling the potential energy of  $n$  molecules uniformly spread over the volume  $v$ ,  $-\frac{a_w}{v}$ , with  $a_w$  constant, we may write the whole potential energy contained in the element  $dv_1$  as  $-\frac{a_w n_1^2}{n^2 dv_1}$ . The condition for the energy then becomes

<sup>1)</sup> L. S. ORNSTEIN. Diss. 1908, p. 60.

$$u = \sum_{dv} \sum_{dw} n_{11} u_{w1} - \sum_{dv} \frac{a_w n_1^2}{n^2 dv_1} = \text{const.}, \quad (7)$$

in which  $u_{w1} = \frac{1}{2} m (\xi_1^2 + \eta_1^2 + \zeta_1^2)$  represents the kinetic energy of translation of a molecule whose velocity lies in  $dw_1$ .

The condition for a maximum, in conjunction with (7) and  $n = \text{const.}$ <sup>1)</sup> gives

$$- \log_e n_{11} - n_1 \frac{\frac{4}{3} \pi \sigma^3}{dv_1} - h \left( u_{w1} - \frac{2a_w n_1}{n^2 dv_1} \right) + \log_e c = 0, \quad (8)$$

in which  $h$  and  $c$  are constants. A few reductions lead to

$$n_1 = \frac{n}{v} dv_1 \quad (9)$$

and

$$n_{11} = \frac{n}{v} \left( \frac{h m}{2 \pi} \right)^{3/2} e^{-h u_{w1}} dv_1 dw_1,$$

the well known conditions for equilibrium: macroscopically uniform distribution throughout the space, and MAXWELL'S distribution of velocities with the same constant  $h$  for each macro-volume-element. This constant  $h$  can be found by obtaining an expression for the energy  $u$

$$u = \frac{3}{2} \frac{n}{h} - \frac{a_w}{v} \quad (10)$$

From (6) and (9) we obtain for the state of equilibrium

$$\log_e W = n \log_e v - \frac{3}{2} n \log_e h + h u_w - \frac{1}{2} \frac{n}{v} n \frac{4}{3} \pi \sigma^3,$$

in which  $u_w$  represents the total kinetic energy, and certain constants are omitted. In conjunction with (3) this gives

$$s = k_p n \log_e v - \frac{3}{2} k_p n \log_e h + k_p h u_w - \frac{1}{2} \frac{k_p n}{v} n \frac{4}{3} \pi \sigma^3. \quad (11)$$

On eliminating  $h$  between this equation and (10) one obtains a fundamental equation of state expressing  $u$  as a function of  $s$  and  $v$ , or  $s$  as a function of  $u$  and  $v$ , which PLANCK calls the canonical equation of state. On keeping  $v$  constant and differentiating (10) and

(11) with respect to  $h$ , since  $T = \left( \frac{\partial u}{\partial s} \right)_v$  one easily obtains

$$T = \frac{1}{k_p h}, \quad (12)$$

<sup>1)</sup> It will be seen that in the case of the most probable distribution the total momentum and the total moment of momentum vanish for each macro-volume-element. If one wished to evaluate the entropy for states in which these magnitudes were not zero one should have to introduce here suitable conditions to allow for them.

from which with (11) it follows that

$$\psi = u - \frac{s}{k_p h} = -\frac{n}{h} \log_e v + \frac{3}{2} \frac{n}{h} \log_e h - \frac{a_w}{v} + \frac{1}{2} \frac{n}{hv} n \frac{4}{3} \pi \sigma^3.$$

Using (12) and the relation  $k_p = R/n$ , in which  $R$  is the gas constant for the quantity under consideration, this equation is transformed into

$$\psi = -RT \log_e v - \frac{3}{2} RT \log_e T - \frac{a_w}{v} + \frac{RT}{v} b_w, \quad (13)$$

in which  $b_w$  has been written for  $\frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3$  and a linear function of  $T$  has been omitted.

From this equation one obtains the value  $\frac{3}{2} R$  for the specific heat at constant volume, while the thermal equation of state becomes

$$p = \frac{RT}{v} \left( 1 + \frac{b_w}{v} \right) - \frac{a_w}{v^2}.$$

Hence (cf. § 1)

$$B = b_w - \frac{a_w}{RT} \quad \dots \quad (14)$$

§ 4. *The virial-coefficient  $B$  for rigid ellipsoids of revolution subject to VAN DER WAALS attractive forces.*

Determination of the macro-complexion.

We shall first assume that in collision between two ellipsoids the speed of rotation around the axis of revolution can also vary. To make sure that HAMILTON'S equations are sufficient to determine the mutual action of two such ellipsoids (cf. also p. 243 note 3) we shall make it essential that the surfaces of the colliding bodies which we are considering can never exert other than normal forces upon each other at their point of contact. We shall, however, assume that it is found on closer investigation that the surfaces of the ellipsoids are not perfect surfaces of revolution but show, it may be, a universal wave-formation; but in the meantime we shall assume that deviations from the true shape of an ellipsoid of revolution are so small that they may be altogether neglected except in so far as they give rise to a moment around the "axis of revolution" during collision. Hence in formulating the condition that the energy has a given value, we shall also have to allow for the speed of rotation around the axis of revolution. To express that condition, then, it is desirable to determine the macro-complexion as was done in § 3 and also with respect to the speeds of rotation around the three axes of

inertia,  $p_r, q_r, r_r$ , in which  $p_r$  represents the speed of rotation around the axis of revolution.

The group macro-complexion is now determined by specifying that  $n_{111}$  unspecified molecules are present in  $dv_1 dw_1 dw_{r1}$

$$n_{211} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad dv_2 \quad \text{,,} \quad \text{,,} \quad \text{etc.} \quad \dots \quad (15)$$

in which  $dw_{r1}$  represents an element of the space involving the coordinates  $p_r, q_r$ , and  $r_r$ ; these elements are also assumed to be equal.

Determination of the micro-complexion:

For this it is necessary to specify the position of the ellipsoid. To do this choose a fixed system of axes  $XYZ$ , and through the origin draw a line  $OA$  parallel to the axis of revolution; we shall determine the position of the ellipsoid by the angles  $AZX = \varphi$ ,  $AOZ = \theta$  and the angle  $\chi$  between the plane  $AOZ$  and a

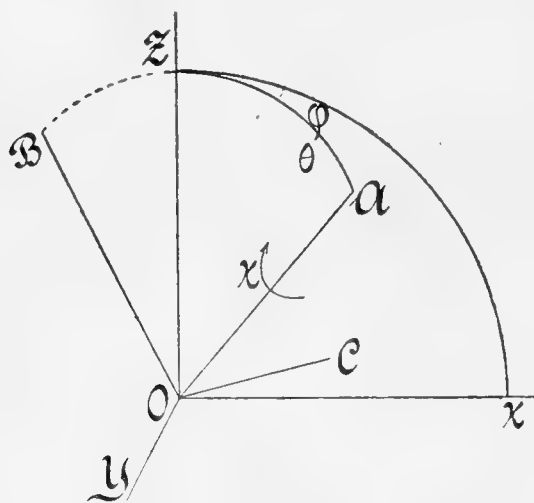


Fig. 1.

fixed meridian plane of the ellipsoid (Fig. 1).

Angular momenta: We may represent the kinetic energy of rotation,  $L_r$ , by the formula

$$L_r = \frac{1}{2} A_r p_r^2 + \frac{1}{2} B_r (q_r^2 + r_r^2), \dots \dots \dots (16)$$

in which  $A_r =$  the moment of inertia about the axis of revolution, and  $B_r =$  ,, ,, ,, ,, ,, an equatorial axis.

We shall choose the equatorial axis to which  $q_r$  refers,  $OB$ , in the plane  $AOZ$ ,  $OC$  perpendicular to  $OA$  and  $OB$  in such a direction that a rotation from  $A$  towards  $B$  seen from  $C$  is in the same direction as a rotation from  $X$  towards  $Y$  seen from  $Z$ .

It is seen that

$$\begin{aligned} p_r &= \dot{\varphi} \cos \theta + \dot{\chi} \\ q_r &= \dot{\varphi} \sin \theta \quad \dots \dots \dots (17) \\ r_r &= -\dot{\theta} \end{aligned}$$

in which the dots represent differentiation with respect to the time.

If we call the angular momenta with reference to  $\varphi, \theta, \chi, \bar{\varphi}, \bar{\theta}, \bar{\chi}$  respectively, we then obtain

$$\begin{aligned} \bar{\varphi} &= A_r \cos \theta \cdot p_r + B_r \sin \theta \cdot q_r, \\ \bar{\theta} &= -B_r r_r, \quad \dots \dots \dots (18) \\ \bar{\chi} &= A_r p_r, \end{aligned}$$

in which  $p_r, q_r$ , and  $r_r$  have the values given in (17).

Instead of determining the micro-complexion by  $d\varphi d\theta d\chi d\bar{\varphi} d\bar{\theta} d\bar{\chi}$  we shall introduce a slight modification. From (18) we find

$$d\bar{\varphi} d\bar{\theta} d\bar{\chi} = A_r B_r^2 \sin \theta dp_r dq_r dr_r,$$

if we stipulate that the sign of equality in this and similar expressions means that in the integral the expression on the left may be replaced by that on the right with the proper modification of the limits of integration.

Let us further write  $do$  for an element of the surface of the sphere of unit radius, by points on which we can indicate the direction of the axis of revolution of the ellipsoid; we then obtain

$$d\varphi d\theta = \frac{do}{\sin \theta}.$$

Hence

$$d\varphi d\theta d\chi d\bar{\varphi} d\bar{\theta} d\bar{\chi} = A_r B_r^2 do d\chi dp_r dq_r dr_r.$$

We shall therefore obtain micro-elements of equal probability (cf. p. 246 note 2) if we measure equal  $d\omega$ 's, equal  $dw$ 's, equal  $do$ 's, equal  $d\chi$ 's and equal  $dw_r$ 's, and combine them.

If each molecule is assigned to a particular micro-element, then the micro-complexion is completely determined.

The number of individual macro-complexions in the group macro-complexion is

$$\frac{n!}{n_{111}! n_{112}! \dots}$$

(compare what was said concerning the corresponding expression in § 3).

The number of micro-complexions in the individual macro-complexion is determined as follows:

The various volume-elements  $dv$  are again independent of each other (cf. § 3). Let us consider the  $n_1$  molecules in  $dv_1$ . To each molecule we ascribe its proper speed of translation  $\xi, \eta, \zeta$  and speed of rotation  $p_r, q_r, r_r$  determined by (15). We then "place" the first molecule in one of the  $v$  elements  $d\chi$ , then in one of the  $x$  elements  $d\omega$  and lastly in one of the  $\mu$  elements  $do$ . This can be done in  $x\mu v$  different ways.

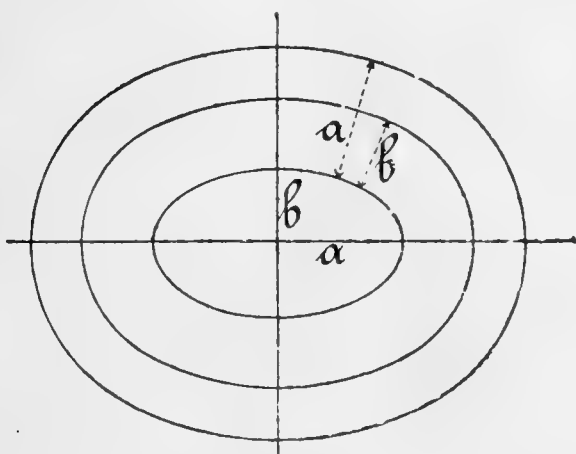


Fig. 2.

We now dispose of the second molecule. For this we have still  $v$  elements  $d\chi$  at our disposal, but for the other coordinates there are fewer places available than was the case with the first molecule. Outwards along the normal to each point of the first ellipsoid mark off a distance  $a$  (equal to half the major axis) (Fig. 2), then each  $d\omega$  outside the surface thus

obtained is a possible position for the centre of the second ellipsoid, and in any of those positions all orientations of the axis of revolution of this ellipsoid are possible. Calling  $v_e$  the volume enclosed by the *outer distance surface* thus obtained, then the above volume-elements give rise to  $\kappa\mu v \left\{ 1 - \frac{v_e}{dv_1} \right\}$  possibilities.

Along the normal to each point of the ellipsoid mark off a distance  $b$  (equal to half the minor axis), we thus obtain a surface within which no centre of another molecule can lie. We shall call this the *inner distance surface*, and designate by  $v_i$  the volume which it encloses. In the shell enclosed between these two distance surfaces the centre of the second ellipsoid can be placed, but then all  $\mu$  orientations *do* are not possible, but only a portion of them, which can be determined in the following fashion (Fig. 3). Let A be the first ellipsoid which we shall regard as immovable. Let  $P$  be a point of the shell determined by the coordinates relative to A:  $\mathbf{x}$  in the direction of the

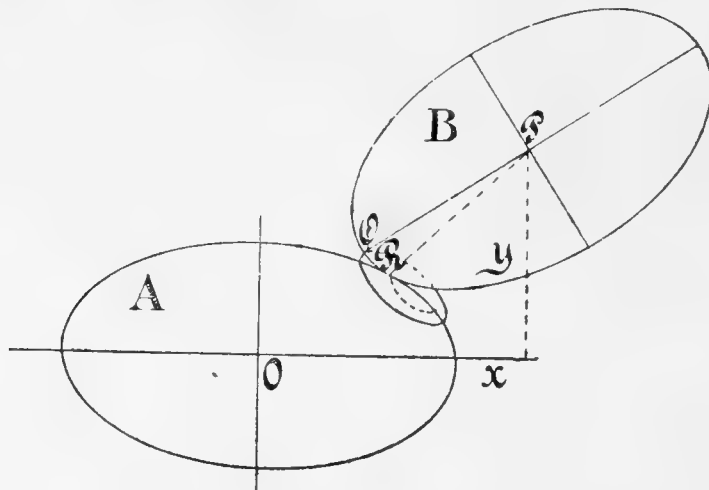


Fig. 3.

axis of revolution,  $\mathbf{y}$  in the direction perpendicular to it. Now place the second ellipsoid with its centre at  $P$ , and, keeping its centre fixed, allow it to roll on the surface of A; during this rolling the point of contact  $R$  describes a trace on the surface of A. We can write for the solid angle of the cone which is described during the rolling by the semi-axis of revolution,  $PQ$ ,  $2\pi\varrho$  if the ellipsoid is prolate,  $2\pi(1-\varrho)$  if oblate, in which  $\varrho$  is a function of  $\mathbf{x}$  and  $\mathbf{y}$ ; there are then  $\mu(1-\varrho)$  orientations  $d\theta$  possible for the ellipsoid B with its centre fixed at  $P$ . Altogether we shall have  $\kappa\mu v \left\{ 1 - \frac{\beta}{dv_1} \right\}$  cases, where

$$\beta = v_i + \int \varrho d\omega. \quad \dots \dots \dots (19)$$

the integration being taken throughout the shell.

$\beta$  may be regarded as the mass obtained taking the volume contained within the inner distance surface as having unit density, and adding to it the sum of the volume-elements contained within the shell between the two surfaces, each multiplied by its own density  $\rho$ .

The placing of the third molecule can be done in  $\kappa_{\mu\nu} \left\{ 1 - 2 \frac{\beta}{dv_1} \right\}$  ways if one takes no account of the complication introduced by the approach of three molecules (cf. § 3). Finally we get

$$W = (\kappa_{\mu\nu})^n \frac{n!}{n_{111}! \dots} \prod_{dv} \prod_{\iota=1}^{\iota=n-1} \left\{ 1 - \iota \frac{\beta}{dv_1} \right\}.$$

Omitting constants this gives

$$\log_e W = - \sum_{d.} \sum_{dv} \sum_{dv_r} n_{111} \log_e n_{111} - \sum_{dv} \frac{n_1^2}{2} \frac{\beta}{dv_1}.$$

Subsequent treatment of this problem differs from that given in § 3 only in so far as the energy condition, under the same assumption as was there made regarding the potential energy, must now be written

$$\begin{aligned} \sum_{dv} \sum_{dv} \sum_{dv_r} n_{111} \left\{ \frac{1}{2} m (\tilde{s}_1^2 + \eta_1^2 + \zeta_1^2) + \frac{1}{2} A_r p_r^2 + \frac{1}{2} B_r (q_r^2 + r_r^2) \right\} - \\ - \sum_{dv} \frac{a_w n_1^2}{n^2 dv_1} = \text{const.} \dots \dots \dots (20) \end{aligned}$$

The result then follows that the specific heat at constant volume for these rigid (but not smooth) ellipsoids is  $3R$ , while as regards the thermal equation of state equation (14) gives the value of  $B$  if we substitute

$$b_w = \frac{n\beta}{2} \dots \dots \dots (21)$$

As far then as concerns the term with the virial-coefficient  $B$ , we find the same equation of state as for rigid spheres<sup>1)</sup>, only with the ellipsoids,  $b_w$  is not such a simple function of the volume of the molecules as with rigid spheres.

We shall now introduce the assumption that the ellipsoids are perfectly *smooth*, so that the velocities of rotation around the axis of revolution undergo no change on collision. We shall also assume that the attractive forces cause no modification in these angular speeds. In that case it is not necessary to allow for the value of

<sup>1)</sup> This may be regarded as a particular case of the general proposition indicated by BOLTZMANN (Gastheorie II §61), for molecules which behave as solid bodies of shape other than spherical.

$p_r$  in the equation for the constant energy; hence we shall also take no account of  $p_r$  in the determination of the macro-complexion.

The group macro-complexion is then specified thus:

$$\begin{array}{l}
 n_{111} \text{ unspecified molecules are present in } dv_1 \, dv_1 \, (dq_r \, dr_r)_1 \\
 n_{112} \quad \quad \quad \text{''} \quad \quad \quad \text{''} \quad \quad \quad \text{''} \quad \quad \quad \text{''} \quad \quad \quad \text{''} \quad \quad \quad \text{''} \quad \quad \quad \text{''} \quad \quad \quad \text{etc. . . .} \quad (22)
 \end{array}$$

in which  $(dq_r \, dr_r)_1$  represents one of the different elements (supposed equal) of the space involving the coordinates  $q_r$  and  $r_r$ . The equation for given energy then becomes

$$\Sigma n_{111} \left\{ \frac{1}{2} m (\xi_1^2 + \eta_1^2 + \zeta_1^2) + \frac{1}{2} B_r (q_{r1}^2 + r_{r1}^2) \right\} - \sum_{dv} \frac{a_w n_1^2}{n^2 dv_1} = \text{const.}$$

As far as the thermal equation of state is concerned the result is the same as that obtained for rough ellipsoids, but the specific heat at constant volume is different, viz.  $\frac{5}{2} R$ , for smooth ellipsoids.

**Physics.** — *On the deduction from BOLTZMANN'S entropy principle of the second virial-coefficient for material particles (in the limit rigid spheres of central symmetry) which exert central forces upon each other and for rigid spheres of central symmetry containing an electric doublet at their centre.* By Dr. W. H. KEESOM. Supplement N<sup>o</sup>. 24<sup>b</sup> to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of April 26, 1912).

§ 5<sup>1</sup>) *The deduction of the second virial-coefficient, B, for material points (in the limit rigid spheres of central symmetry) which exert central forces upon each other.*

In this section we shall deduce the equation of state, as far as the second virial-coefficient,  $B$ , is concerned (cf. § 1), for a system of molecules which act upon each other as if they were material particles (in the position of the centres, which are also the centres of gravity of those molecules) and with forces which are given invariable functions of the distance. All mutual actions other than that just described will be excluded. The case in which the spheres can be regarded as rigid spheres of central symmetry (§ 3) exerting central attractive or repulsive forces upon each other which are a function of the distances between their centres, will be treated as a limiting case.

<sup>1</sup>) To facilitate reference to Suppl. N<sup>o</sup>. 24<sup>a</sup> sections, equations and diagrams in the present paper are numbered as continuations of those in Suppl. N<sup>o</sup>. 24<sup>a</sup>.



This problem has already been discussed by BOLTZMANN<sup>1)</sup> and by REINGANUM<sup>2)</sup>, both of whom applied BOLTZMANN'S distribution law to the deduction of the pressure from the equation of the virial, and by ORNSTEIN<sup>3)</sup>, who used GIBBS'S methods of statistical mechanics. In this § our treatment of the problem will be based upon the BOLTZMANN entropy principle, and at the same time we shall obtain an expression for the BOLTZMANN  $H$ -function for this case, while the BOLTZMANN distribution law for this case will also result. In § 6 we shall conclude with a discussion of a system of rigid molecules of central symmetry, each with an electric doublet at its centre.

The reader is referred to Suppl. N<sup>o</sup>. 24*a*, § 2 and 3 for a general exposition of the method which forms the basis of the present investigation, and for an application of this method to rigid spheres of central symmetry exerting VAN DER WAALS attractive forces upon each other.

In the case now under discussion the macro-complexion must first be determined as in § 3 by the conditions laid down in (4). In order to be in a position, however, to write down the energy equation for the present problem it is necessary to know how many pairs there are amongst those molecules, the distances between whose centres lie between certain definite limits. We shall assume that we have to differentiate only between molecules within whose sphere of influence are no other molecules and those within whose sphere of influence one other molecule is present; that is, that molecules which have two or more other molecules within their sphere of influence are of such infrequent occurrence in those states of the molecular system which we shall consider, that we may entirely neglect their influence. This supposes that the force exerted by any molecule is appreciable only over a finite sphere of influence which is small compared with the space in which the molecules are moving. We assume that the elements,  $dv$ , which are taken to determine the macro-complexion (cf. § 3) are large compared with this sphere of influence. We now divide the radius of the sphere of influence,  $\tau$ , into a great number of equal elements  $dr_1, dr_2$ , etc., which are so small that we may neglect the change in the potential energy of a pair of molecules during a change equal to one of these elements in the distance separating them. We shall subdivide the  $n_{11}$  molecules contained in  $dv, dv_1$  into

<sup>1)</sup> L. BOLTZMANN. Wien Sitz.-Ber. [2*a*] 105 (1896), p. 695, Wiss. Abh. 3, p. 547. In that paper the general result is also applied to the special case of repulsive forces varying as  $Kr^{-5}$ .

<sup>2)</sup> M. REINGANUM. Ann. d. Phys. (4) 6 (1901), p. 533.

<sup>3)</sup> L. S. ORNSTEIN. Diss. Leiden 1908, p. 70 sqq.

- $n_{11a}$  single molecules (with no other molecule within their sphere of influence)  
 $n_{11b1}$  molecules belonging to pairs which are separated by a distance lying between  $r_1$  and  $r_1 + dr_1$ ,  
 $n_{11b2}$  molecules belonging to pairs separated by a distance lying between  $r_2$  and  $r_2 + dr_2$ , etc., . . . . . (23)  
 the  $n_{12}$  molecules in  $dv_1 dv_2$  we shall subdivide into  
 $n_{12a}$  single molecules etc.

The group micro-complexion is determined by these numbers  $n_{11a}$  etc., when no account is taken of the individuality of the molecules.

Determination of the micro-complexion:

Each of the equal elements  $dv$  is divided into  $\kappa$  equal volume-elements  $d\omega$  whose linear dimensions are still small in comparison with the  $dr_1$  etc. which we have just introduced. Otherwise the determination of the micro-complexion is just the same as in § 3.

The number of individual macro-complexions in the group macro-complexion is

$$\frac{n!}{n_{11a}! n_{11b1}! n_{11b2}! \dots n_{12a}! \dots}$$

The number of micro-complexions in the individual macro-complexion is found in this way: All the volume-elements  $dv_1$  etc. are independent of each other, so that we can obtain the total number of micro-complexions by finding the number for each volume-element  $dv_1$  and multiplying these together. We shall first assign to each of the

$$n_1 = n_{11a} + n_{11b1} + n_{11b2} + \dots + n_{12a} + \dots \quad (24)$$

molecules in  $dv_1$  its place in the micro-volume-elements  $d\omega_{11} \dots d\omega_{1\kappa}$ , and thereafter give it its proper speed as obtained in the determination of the individual macro-complexion. The latter operation will not give rise to any change in the number of micro-complexions.

In  $dv_1$  therefore we have got to place

$n_1$  specified molecules.

Of these:

$n_{1a}$  specified molecules are to be single

$n_{1b1}$  ,, ,, are to belong to pairs whose distance apart lies between  $r_1$  and  $r_1 + dr_1$ ,

$n_{1b2}$  etc.,

where

$$\left. \begin{aligned} n_{1a} &= n_{11a} + n_{12a} + \dots \\ n_{1b1} &= n_{11b1} + n_{12b1} + \dots \end{aligned} \right\} \dots \dots \dots (25)$$

The first of the  $n_{1a}$  molecules gives rise to  $\kappa$  possibilities according to which of the  $\kappa$  elements  $d\omega$  it is placed in. When the first

molecule has been placed there is a volume  $dv_1 \left\{ 1 - \frac{\frac{4}{3} \pi \tau^3}{dv_1} \right\}$  left available for the second of the  $n_{1a}$  single molecules. The second molecule, therefore, gives rise to the factor  $\kappa \left\{ 1 - \frac{\frac{4}{3} \pi \tau^3}{dv_1} \right\}$  in the number of micro-complexions. The third of the  $n_{1a}$  molecules gives  $\kappa \left\{ 1 - 2 \cdot \frac{\frac{4}{3} \pi \tau^3}{dv_1} \right\}$ ; in this no account is taken of the fact that in a number of micro-complexions the spheres of influence of the first two molecules partially overlap, as these complications need only be allowed for in the calculation of the  $C$  and subsequent virial-coefficients (cf. § 3). Proceeding in this fashion the  $n_{1a}$  single molecules give the factor

$$\kappa^{n_{1a}} \prod_{i=1}^{i=n_{1a}-1} \left\{ 1 - i \frac{\frac{4}{3} \pi \tau^3}{dv_1} \right\}.$$

We must now place the  $n_{1b1}$  molecules which belong to pairs whose distance apart lies between  $r_1$  and  $r_1 + dr_1$ . In order to see in how many different ways this may be done we must first notice that one of these molecules can go to form a pair whose distance apart lies between the proper limits only in combination with another of the same group (this does not strictly hold if the molecule in question is placed on the boundaries of  $dv_1$ ; if  $n_1$  is sufficiently great, however, the effect of this may be neglected). The  $n_{1b1}$  molecules can then combine to form pairs in

$$\frac{n_{1b1}!}{2^{\frac{n_{1b1}}{2}} \left( \frac{n_{1b1}}{2} \right)!}$$

different ways. Let us take one of these combinations. Take one of the pairs and place it; this is done by first assigning a place to one of the pair. As it must be placed outside the sphere of influence of any of the  $n_{1a}$  single molecules already in position there are left

$$\kappa \left\{ 1 - n_{1a} \frac{\frac{4}{3} \pi \tau^3}{dv_1} \right\}$$

places available. Having placed the first molecule of the pair in

question in one of these places there are, since the second of the pair must come within a distance between  $r_1$  and  $r_1 + dr_1$  of the first,

$$\propto \frac{4\pi r_1^2 dr_1}{dv_1}$$

places available. This is so at least for all those cases in which the first molecule is placed within a distance not less than  $\tau + r_1$  of any of the  $n_{1a}$  molecules already in position. When that distance is not exceeded complications are introduced by the fact that a portion of the shell  $4\pi r_1^2 dr_1$  lies within the sphere of influence of that other molecule. If we wished to confine ourselves strictly to cases in which one molecule is acted upon at any time by no more than one other molecule, then these portions of the shell which are overlapped by other spheres of influence ought not to be included in the summation.

But cases in which these complications occur form but a small fraction of the whole, both for this and for subsequent pairs of

molecules, the order of magnitude being  $\frac{n_1 \cdot \frac{4}{3} \pi \tau^3}{dv_1}$ , which is very

small. The terms  $\propto \frac{4\pi r_1^2 dr_1}{dv_1}$  give rise to terms in  $\log_e W$  which are of the first order of small quantities, and which we shall have to take into account. Subsequent terms, however, may be omitted, and in that case we may also neglect the effects of the complication referred to above. Likewise we shall for the same reason neglect corresponding complications for subsequent pairs, of which the placing of the first molecule already gives rise to a factor which we change in a corresponding manner.

As the method here described gives all the positions possible, after the  $n_{1a}$  single molecules have been disposed of, for the first pair of molecules whose distance apart lies between  $r_1$  and  $r_1 + dr_1$ , the placing of this pair gives rise to

$$\propto^2 \left\{ 1 - n_{1a} \frac{\frac{4}{3} \pi \tau^3}{dv_1} \right\} \frac{4\pi r_1^2 dr_1}{dv_1}$$

possibilities. In this expression we shall introduce a factor  $1 - (n_{1a} + 1) \frac{\frac{4}{3} \pi \tau^3}{dv_1}$ ; these factors, too, of which there is one for each pair of mo-

lecules, do not influence terms of the first order of small quantities.

By treating all the pairs of molecules contained in  $dv_1$  in the same way, and then all the pairs of molecules in  $dv_2$  etc., we obtain for the number of micro-complexions in the group macro-complexion

$$W = x^n \frac{n!}{n_{11a}! n_{11b1}! \dots n_{12a}! \dots} \prod_{\nu=1}^{i=n_1-1} \prod_{\nu=1} \left\{ 1 - \nu \frac{\frac{4}{3} \pi \tau^3}{dv_1} \right\} \cdot \prod_{dr} \frac{n_{1b1}!}{2^{\frac{n_{1b1}}{2}} \left(\frac{n_{1b1}}{2}\right)!} \left(\frac{4\pi r_1^2 dr_1}{dv_1}\right)^{\frac{n_{1b1}}{2}} \dots \dots \dots (26)$$

Retaining the principal and first order terms in the expression for  $\log_e W$ , and abandoning higher orders of small quantities as well as all terms which remain constant under all the considerations involved, we obtain the expression

$$\log_e W = -n_{11a} \log_e n_{11a} - n_{11b1} \log_e n_{11b1} \dots - \sum_{dv} \frac{n_1^2}{2} \frac{\frac{4}{3} \pi \tau^3}{dv_1} + \sum_{dv} \sum_{dr} \left[ \frac{n_{1b1}}{2} \log_e n_{1b1} - \frac{n_{1b1}}{2} + \frac{n_{1b1}}{2} \log_e \left(\frac{4\pi r_1^2 dr_1}{dv_1}\right) \right] \dots \dots (27)$$

If the sign of this expression is changed, it becomes a form of the BOLTZMANN  $H$ -function for this case.

The state of equilibrium:

Let us write  $-\varphi(r_1)$  for the potential energy as dependent upon the mutual forces exerted by a pair of molecules at a distance  $r_1$  apart, and let us assume that for separating distances greater than  $\tau$  the potential energy of a pair of molecules may be taken to be  $= 0$ ; we may then write the energy condition in the form

$$u = \sum_{dv} \sum_{dw} n_{11} u_{w1} - \frac{1}{2} \sum_{dv} \sum_{dr} n_{1b1} \varphi(r_1) = \text{const.} \dots \dots (28)$$

(for the significance of  $u_{w1}$  cf. § 3).

The condition that  $\log_e W$  is a maximum together with this equation (28), and the condition  $n = \text{const.}$ , and equations (24) and (25) give

$$\left. \begin{aligned} -\log_e n_{11a} - n_1 \frac{\frac{4}{3} \pi \tau^3}{dv_1} - h u_{w1} + \log_e c &= 0 \\ -\log_e n_{11b1} - n_1 \frac{\frac{4}{3} \pi \tau^3}{dv_1} + \frac{1}{2} \log_e n_{1b1} + \frac{1}{2} \log_e \left(\frac{4\pi r_1^2 dr_1}{dv_1}\right) - \\ - u_{w1} - h \left\{ \frac{1}{2} \varphi(r_1) \right\} + \log_e c &= 0 \end{aligned} \right\} \dots \dots (29)$$

etc., in which  $c$  and  $h$  are constants. If we retain only the terms of the rank of principal or first order terms in  $\log_e W$ , we get, since  $n_1 \frac{4}{3} \pi r^3$  is small compared with  $dv_1$ :

$$\left. \begin{aligned} n_{11a} &= c \left\{ 1 - n_1 \frac{\frac{4}{3} \pi r^3}{dv_1} \right\} e^{-hu_{w1}} \\ n_{11b1} &= c \left( n_{1b1} \frac{4\pi r_1^2 dr_1}{dv_1} \right)^{1/2} e^{-h\{u_{w1} - \frac{1}{2}\varphi(r_1)\}} \end{aligned} \right\} \dots (30)$$

The constant  $c$  is determined by the condition that the total number of molecules must be equal to  $n$ . Let us write  $c = c' dv_1 = c' d\zeta_1 d\eta_1 d\xi_1$ , and then summation (integration) of (30) with respect to  $dv_1$  gives

$$n_{1b1} = c'^2 \left( \frac{2\pi}{hm} \right)^3 \frac{4\pi r_1^2 dr_1}{dv_1} e^{h\varphi(r_1)}.$$

Summation with respect to  $r_1$  and addition of the value of  $n_{1a}$  yields an expression for  $n_1$  which leads to the conclusion that the distribution of the molecules in space in the state of equilibrium is uniform in the macroscopic sense.  $c'$  is next determined by summation with respect to  $dv_1$ . We then obtain

$$n_{1b1} = \frac{n^2}{v^2} 4\pi r_1^2 dr_1 e^{h\varphi(r_1)} dv_1 \dots (31)$$

If we divide this by 2 it gives us, to a first approximation, the number of pairs of molecules whose distance apart lies between  $r_1$  and  $r_1 + dr_1$  in the state of equilibrium. This expression is in agreement with that given by BOLTZMANN (p. 257 note 1) which was also used by REINGANUM (p. 257 note 2).

We find, moreover, that

$$n_{11b1} = \frac{n^2}{v^2} \left( \frac{hm}{2\pi} \right)^{3/2} 4\pi r_1^2 dr_1 e^{-h\{u_{w1} - \varphi(r_1)\}} dv_1 dw_1, \dots (32)$$

so that the velocity distribution is the same for molecules in each other's neighbourhood as for single molecules.

For the number of single molecules we get

$$n_{11a} = \frac{n}{v} \left( \frac{hm}{2\pi} \right)^{3/2} \left\{ 1 - \frac{n}{v} P \right\} e^{-hu_{w1}} dv_1 dw_1, \dots (33)$$

in which

$$P = \int_0^{\tau} e^{h\varphi(r)} 4\pi r^2 dr \dots (34)$$

if we replace summation with respect to  $dr$  by an integration.

To determine  $h$  we derive the total energy,  $u$ ,

$$u = \frac{3n}{2h} - \frac{1}{2} \frac{n^2}{v} \cdot Q, \quad \dots \dots \dots (35)$$

in which

$$Q = \int_0^\tau e^{h\varphi(r)} \varphi(r) \cdot 4\pi r^2 dr. \quad \dots \dots \dots (36)$$

If we now calculate the expression for  $\log_e W$  from (27), allowing for (33), (32) and (31), retaining only principal and first order terms we get from (3) and (35) for the state of equilibrium

$$s = nk_P \ln v - \frac{3}{2} nk_P \ln h + k_P hu - \frac{1}{2} k_P \frac{n^2}{v} \left( \frac{4}{3} \pi \tau^3 - P \right) \quad (37)$$

On elimination of  $h$  by means of (35) this equation yields what PLANCK calls the canonical equation of state. And just as in § 3, noting that  $P$  and  $Q$  are related to each other by the equation  $Q = \frac{dP}{dh}$  we now recover equation (12) from (35) and (37), a result to be expected and consequently affording a desirable control.

Introducing the temperature  $T$  as defined by (12) and also the gas constant  $R$  (cf. § 3) we obtain

$$\psi = -RT \log_e v - \frac{3}{2} RT \log_e T + \frac{RT}{v} \cdot \frac{n}{2} \left( \frac{4}{3} \pi \tau^3 - P \right) \quad (38)$$

The specific heat at constant volume  $\gamma_v$  is now found to be dependent upon the volume. Putting  $v = \infty$  in the expression for  $\gamma_v$  we obtain the specific heat at constant volume in the AVOGADRO state<sup>1)</sup>  $\gamma_{v\Lambda} = \frac{3}{2} R$ .

For the thermal equation of state we obtain

$$p = \frac{RT}{v} \left\{ 1 + \frac{B}{v} \right\}, \quad \dots \dots \dots (39)$$

with the second virial coefficient

$$B = \frac{1}{2} n \int_0^\tau \left\{ 1 - e^{h\varphi(r)} \right\} 4\pi r^2 dr \quad \dots \dots \dots (40)$$

in which  $h$  may be replaced by  $\frac{1}{k_p T}$ <sup>2)</sup>.

<sup>1)</sup> Cf. Suppl. N<sup>o</sup>. 23, Nr. 39a.

<sup>2)</sup> This result agrees with that given by ORNSTEIN, Thesis for the Doctorate, p. 73.

By introducing for  $\varphi(r)$  a definite function which vanishes for  $r > \tau$ , or, at least approximates to zero with sufficient rapidity as  $r$  increases, we should obtain from (40) the value of the virial-coefficient  $B$  for that particular law of force. The case mentioned in the beginning of this section of molecules which can be regarded as rigid spheres of central symmetry exerting upon each other central attractive forces<sup>1)</sup> which are a function of the distances between their centres, can be obtained from this result by allowing  $\varphi(r)$  to approximate to  $-\infty$  for  $r$  less than  $\sigma$  ( $\sigma =$  diameter of a molecule). We then get

$$B = \frac{1}{2} n \left\{ e^{hv} \frac{4}{3} \pi \sigma^3 + h \int_{\sigma}^{\tau} e^{h\varphi(r)} \varphi'(r) \cdot \frac{4}{3} \pi r^3 dr \right\}, \quad (41)$$

in which  $v = \varphi(\sigma)$ , so that  $-v$  represents the potential energy of a pair of molecules which are in contact.

In this expression for  $B$  the first term represents the collision virial which, as first shown by REINGANUM, becomes, on account of the attractive forces,  $e^{hv}$  times greater than the value found in § 3; the second term represents the attraction virial, and is negative since  $\varphi'(r)$  is negative for attraction.

For  $\varphi(r) = \frac{c}{r^q}$ , in which  $q$  is greater than 3, and for which

$v = \frac{c}{\sigma^q}$ , this becomes

$$B = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \left\{ 1 - \frac{3}{q-3} hv - \frac{1}{2!} \frac{3}{2q-3} (hv)^2 - \frac{1}{3!} \frac{3}{3q-3} (hv)^3 \dots \right\}, \quad (42)$$

which gives, on replacing  $h$  by  $\frac{1}{k_p T}$ , a series of ascending powers of  $T^{-1}$ .

§ 6. *The virial-coefficient  $B$  for rigid smooth molecules of central symmetry, having at their centres an electric doublet of constant moment.*

In this section we shall regard the molecules as rigid smooth

<sup>1)</sup> These formulae also hold for repulsive forces and for forces which are for certain distances attractive, for others repulsive.

<sup>2)</sup> The force which two molecules exert upon each other as a whole is then proportional to  $r^{-(q+1)}$ . On the supposition of forces operating according to the above law between the volume-elements of spherical molecules supposed homogeneous the resultant could not be regarded as a function  $r^{-q}$  (with  $q$  constant) of the distance between the centres.



spheres of central symmetry, each having at its centre an electric doublet; we shall assume that the distance between the two poles of the doublet is negligible compared with the dimensions of the molecule, while the moment of the doublet is nevertheless so large that it must be allowed for by introducing terms into the equation of state to represent the mutual action between the doublets. In all considerations introduced into the present section we shall regard the moment of the doublet as constant. A model of a molecule which, in so far as its external action is concerned, could be regarded as approximating closely to such a doublet, would be given by a non-conducting sphere with a uniform distribution of positive electricity (or with the charge distributed in concentric shells, each of constant density) in which there is an immovable electron at a very small distance from the centre (the centre coinciding with the centre of gravity). The terminology of this section, however, will be chosen with reference to the supposition of two poles infinitely close to each other (electric doublet) at the centre of the sphere. External action will be calculated as if only electrostatic forces were involved. In this supposition the mutual action of two molecules may be treated as being governed by the HAMILTON equations. The assumption would have to be more closely verified in the further development of the theory of the action of a model such as the one just described.

VAN DER WAALS Jr.<sup>1)</sup> has considered such a system as the one here described, and calculated the mean attraction between two molecules when these have assumed orientations with respect to the axes of the doublets which are in accord with the condition for heat equilibrium; he showed that the law of decrease of this attraction with increasing distance must be more rapid than  $r^{-4}$ .

The object of the present section is to deduce the virial-coefficient  $B$  by the method indicated in § 2.

The group macro-complexion is first determined by (22) as in the treatment for smooth ellipsoids in § 4.

In order to be able to evaluate the potential energy it is necessary to subdivide the  $n_1$  molecules present in the volume-element  $dv_1$  into  $n_{1a}$  single molecules (cf. § 5), and  $n_{1b}$  molecules which belong to molecular pairs, and exert forces upon each other of such magnitude that they must be allowed for in the determination of  $B$ . We shall once more assume that cases in which one molecule is acted upon by more than one other molecule with forces sufficiently

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<sup>1)</sup> J. D. VAN DER WAALS Jr., These Proceedings June, Oct. 1908, March 1912.

large to influence the result are of such rare occurrence that they may be neglected altogether. In so far as the fact that the field of a doublet does actually extend to infinity introduces difficulties into the treatment, we shall, where necessary, conceive that the field is annihilated at distances greater than  $r = \infty$  so that we may regard  $r$  as the radius of the sphere of influence of the doublet.

The  $\frac{n_{1b}}{2}$  pairs we shall have to separate into various groups. We shall determine a definite pair of molecules in the following way:

1 by the distance  $r$  between the centres,

2 by the angles  $\theta_1$  and  $\theta_2$ , which the axes of the doublets make with the line joining their centres. In this we shall choose the direction of a line joining the centres of two molecules as positive for the first molecule when it goes towards the other, and as positive direction of the axis of the doublet the direction towards the positive pole. The angle concerned will be taken as lying between 0 and  $\pi$ ;

3 by the angle  $\varphi$  between the two planes each of which contains the axis of one of the doublets and the line joining their centres.

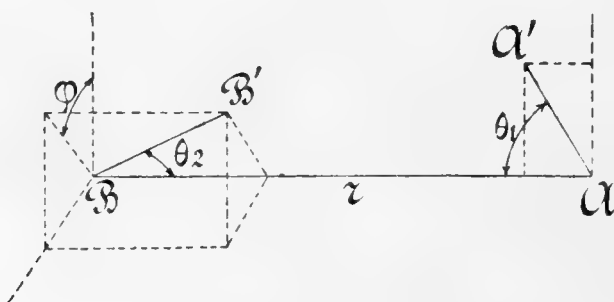


Fig. 4.

Values lying between 0 and  $2\pi$  will be given to this angle. We can specify the angle  $\varphi$  uniquely for any pair of doublets in the following way: Let  $AA'$  and  $BB'$  (fig. 4) represent the pair of doublets,  $A$  and  $B$  being the centres of the molecules, and  $A'$  and  $B'$  being in the positive direction along the axes of the doublets. Let us now take up our position either at  $A$  or  $B$ , say at  $A$ , and project  $AA'$  and  $BB'$  upon a plane passing through  $B$  and perpendicular to  $AB$ ; the angle  $\varphi$  is then that angle through which the projection of  $BB'$  must turn in the positive direction as seen from  $A$  in order to coincide with the projection of  $AA'$ .

The number of pairs of molecules which "are present" in a definite element of the space determined by the coordinates  $r$ ,  $\theta_1$ ,  $\theta_2$ ,  $\varphi$ , that is to say, the number of molecule pairs with a definite "space freedom  $(dr d\theta_1 d\theta_2 d\varphi)_1$ " we shall indicate by putting the

number corresponding to this freedom immediately after the index  $b$ .

The group macro-complexion is then determined as follows :

$$\text{in } dv_1 \, dw_1 \, (dq_r \, dr_r)_1 \quad \left. \begin{array}{l} \text{“there are” } n_{111a} \text{ single molecules} \\ n_{111b1} \text{ molecules belong-} \\ \text{ing to pairs of molecules with} \\ \text{the freedom } (dr \, d\theta_1 \, d\theta_2 \, d\varphi)_1, \text{ etc.} \end{array} \right\} \quad (43)$$

Determination of the micro-complexion :

For this as in the treatment of smooth ellipsoids at the conclusion of § 4 we subdivide the respective spaces into equal  $d\omega$ 's, equal  $dw$ 's, equal  $do$ 's, equal  $d\chi$ 's, equal  $dp_r$ 's and equal  $(dq_r \, dr_r)$ 's. If these are determined for the position of each molecule, we have then a definite micro-complexion. We may refer to § 4 for the proof that the micro-complexions thus determined represent cases of equal probability.

The number of individual macro-complexions in the group macro-complexion is

$$\frac{n!}{n_{111a}! \, n_{111b1}! \, \dots}$$

The number of micro-complexions in the individual macro-complexion:

To determine this the macro-volume-elements are again to be considered as independent of each other. Let  $\varkappa$  represent the number of equal micro-volume-elements  $d\omega_{11} \dots$  in  $dv_1$ ,  $\mu$  the number of equal elements of surface of the unit radius sphere, points on whose surface give the directions of the axes of the doublets,  $\nu$  the number of equal elements  $d\chi$  ( $\chi =$  the angle representing the rotation of the molecule around the axis of the doublet), and  $\nu'$  the number of equal elements  $dp_r$  ( $p_r =$  the speed of rotation around the axis of the doublet).

We shall first ascribe to each molecule its  $d\omega$ , its  $do$ , its  $d\chi$ , and its  $dp_r$  for each micro-complexion; we shall then give it its  $dw$  and its  $dq_r \, dr_r$  as specified by (43). The latter is then without influence upon the number of micro-complexions.

In  $dv_1$  we have to place  $n_1$  specified molecules :

$$n_1 = n_{111} + n_{112} + \dots + n_{121} + \dots \quad (44)$$

Of these  $n_{1a}$  specified molecules are single

$$\begin{array}{l} n_{1b1} \quad \text{,,} \quad \text{,,} \quad \text{belong to pairs with the freedom} \\ \vdots \quad \quad \quad \quad \quad \quad \quad (dr \, d\theta_1 \, d\theta_2 \, d\varphi)_1 \end{array}$$

$$\text{if } \left. \begin{array}{l} n_{1a} = n_{111a} + n_{112a} \dots n_{121a} + \dots \\ n_{1b1} = n_{111b1} + n_{112b1} \dots n_{121b1} + \dots \end{array} \right\} \quad (45)$$

The placing of the  $n_{1a}$  molecules (for the approximation here

employed cf. § 5) gives rise to

$$(\chi\mu\nu\nu')^{n_{1a}} \prod_{\nu=1}^{\nu=n_{1a}-1} \left\{ 1 - \nu \frac{\frac{4}{3}\pi r^3}{dv_1} \right\}$$

possibilities.

Let us now place the  $n_{1b1}$  molecules. Again we may remark that one of these molecules can go to form a pair only with another molecule of the same group. These pairs can be formed in

$$\frac{n_{1b1}!}{2^{\frac{n_{1b1}}{2}} \left( \frac{n_{1b1}}{2} \right)!}$$

different ways (cf. § 5),

Let us consider the first pair of molecules in one of these combinations in particular. For the first molecule there are

$$\chi \left\{ 1 - n_{1a} \frac{\frac{4}{3}\pi r^3}{dv_1} \right\} \mu\nu\nu'$$

places available in the proper space (cf. § 3). When the first molecule has thus been placed and given a definite orientation, there are on account of the freedoms  $d\theta_1 dr$

$$\chi \frac{2\pi r^2 \sin \theta_1 d\theta_1 dr}{dv_1}$$

places in space available for the second molecule. On account of the freedoms  $d\theta_2 d\varphi$  there are

$$\frac{\sin \theta_2 d\theta_2 d\varphi}{d\omega} = \mu \frac{\sin \theta_2 d\theta_2 d\varphi}{4\pi}$$

orientations possible for this second molecule for each of its positions in space.

$\chi$  and  $p_r$  in addition give rise to the factor  $\nu\nu'$ . We thus obtain on the whole

$$(\chi\mu\nu\nu')^2 \left\{ 1 - n_{1a} \frac{\frac{4}{3}\pi r^3}{dv_1} \right\} \frac{r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi}{2 dv_1}$$

possibilities for this pair of molecules, to which we affix the factor

$1 - (n_{1a} + 1) \frac{\frac{4}{3} \pi \tau^3}{dv_1}$ , as was done in § 5. Doing this in turn for the other pairs of molecules, we finally obtain

$$W = (z_{\mu\nu\nu'})^n \frac{n!}{n_{111a}! n_{111b1}! \dots} \prod_{\nu} \prod_{\iota=1}^{\iota=n_{\nu}-1} \left\{ 1 - \iota \frac{\frac{4}{3} \pi \tau^3}{dv_1} \right\} \prod_{r\theta_1\theta_2\varphi} \frac{n_{1b1}!}{2^{\frac{n_{1b1}}{2}} \left(\frac{n_{1b1}}{2}\right)!} \left( \frac{r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi}{2 dv_1} \right)^{\frac{n_{1b1}}{2}}, \quad (46)$$

where  $\prod$  indicates that the product must be taken for all freedoms  $r\theta_1\theta_2\varphi$  (elements in a corresponding space) determined by  $r, \theta_1, \theta_2$  and  $\varphi$  respectively. The notation of this expression has been simplified by omitting the index which is used to indicate the special freedom ( $dr d\theta_1 d\theta_2 d\varphi$ ) except in the notation referring to the number of molecules. From (46) we obtain (cf. § 5 for the omission of terms)

$$\log_e W = -n_{111a} \log_e n_{111a} - n_{111b1} \log_e n_{111b1} \dots - \sum_{\nu} \frac{n_{\nu}^2}{2} \frac{\frac{4}{3} \pi \tau^3}{dv_1} + \sum_{\nu} \sum_{r\theta_1\theta_2\varphi} \left[ \frac{n_{1b1}}{2} \log_e n_{1b1} - \frac{n_{1b1}}{2} + \frac{n_{1b1}}{2} \log_e \left( \frac{r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi}{2 dv_1} \right) \right] \quad (47)$$

Changing the sign we obtain an expression for the BOLTZMANN  $H$ -function for this system.

The equilibrium state:

The energy condition gives

$$u = \sum_{\nu} \sum_{\nu'} (n_{111a} + n_{111b1} + \dots) u_{w11} + \sum_{\nu} \sum_{r\theta_1\theta_2\varphi} n_{1b1} u_{1b} = \text{const.} \quad (48)$$

where

$u_{w11} = \frac{1}{2} m (\xi_1^2 + \eta_1^2 + \zeta_1^2) + \frac{1}{2} B_r (q_{r1}^2 + r_{r1}^2)$  represents the kinetic and  $u_{1b} = \frac{m_e^2}{r^3} (2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \varphi)$  the potential energy

$m$  is the mass of a molecule,  $B_r$  the moment of inertia around an axis perpendicular to the axis of the doublet, and  $m_e$  the moment of the doublet. From the condition for a maximum value of  $\log_e W$ , together with the conditions (48) and  $n = \text{const.}$  and the equations

(44) and (45) the deduction of the distribution in the state of equilibrium and the calculation of the entropy are *mutatis mutandis* made as in § 5. We shall give only the following results:

The number of pairs of molecules with freedoms  $dr, d\theta_1, d\theta_2, d\varphi$  is obtained from

$$n_{1b1} = \frac{n^2}{v^2} e^{-hu_{b1}} \frac{r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi}{2} dv_1 \dots \quad (49)$$

on division by 2.

From

$$n_{111b1} = \frac{n^2}{v^2} \left(\frac{hm}{2\pi}\right)^{3/2} \frac{hB_r}{2\pi} e^{-h(u_{w11} + u_{b1})} \frac{r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi}{2} dv_1 dw_1 dq_{r1} dr_{r1} \quad (50)$$

it follows that the distribution of the velocities (including  $q_r$  and  $r_r$ ) is independent of the position of the molecules relative to each other.

We also find that

$$n_{111a} = \frac{n}{v} \left(\frac{hm}{2\pi}\right)^{3/2} \frac{hB_r}{2\pi} \left\{ 1 - \frac{n}{v} \cdot P \right\} e^{-hu_{w11}} dv_1 dw_1 dq_{r1} dr_{r1}, \quad (51)$$

in which

$$P = \frac{1}{2} \int_0^\tau \int_0^\pi \int_0^\pi \int_0^{2\pi} e^{-hu_{b1}} r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi, \quad (52)$$

where the summation with respect to  $r, \theta_1, \theta_2, \varphi$  has been replaced by a corresponding integration.

Macroscopically the distribution throughout space is uniform.

Elimination of  $h$  from

$$\left. \begin{aligned} s &= nk_P \ln v - \frac{5}{2} n k_P \ln h + k_P h u + \frac{1}{2} k_P \frac{n^2}{v} P - k_P \frac{n^2}{2v} \cdot \frac{4}{3} \pi \tau^3 \\ \text{and} \\ u &= \frac{5n}{2h} + \frac{1}{2} \frac{n^2}{v} Q, \dots \dots \dots \end{aligned} \right\} \quad (53)$$

in which

$$Q = \frac{1}{2} \int_0^\tau \int_0^\pi \int_0^\pi \int_0^{2\pi} e^{-hu_{b1}} u_{b1} r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi \dots \dots \quad (54)$$

gives the canonical equation of state.

From (53) we again obtain  $T = \frac{1}{k_P h}$ .

The specific heat at constant volume in the AVOGADRO state,  $\gamma_{c\Delta}$ ,

becomes  $\frac{5}{2} R$ , in agreement with the circumstance that both  $q_r$  and  $r_r$ , but not  $p_r$ , participate in the heat equilibrium in consequence of the torques exerted by the doublets upon each other.

For the thermal equation of state we again get (39), with  $B$  now equal to

$$B = \frac{1}{2} n \left( \frac{4}{3} \pi \sigma^3 - P' \right), \quad . . . . . (55)$$

in which

$$P' = \frac{1}{2} \int_{\sigma}^{\tau} \int_0^{\pi} \int_0^{\pi} \int_0^{2\pi} (e^{-hu_{\theta 1}} - 1) r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi . . . (56)$$

$P'$  is convergent for  $\tau = \infty$ , so that as far as (55) is concerned the assumption is no longer necessary that the field of the doublet is annihilated at distances greater than  $\tau$  (the same is true for (53) if  $P'$  is introduced in the expression for  $s$ ).

In order to evaluate the integral  $P'$  we shall write  $2 \cos \theta_1 = g \cos \psi$  and  $\sin \theta_1 = g \sin \psi$  ( $g \geq 0$ ,  $0 < \psi < \pi$ ), so that

$$2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \varphi = g (\cos \psi \cos \theta_2 + \sin \psi \sin \theta_2 \cos \varphi).$$

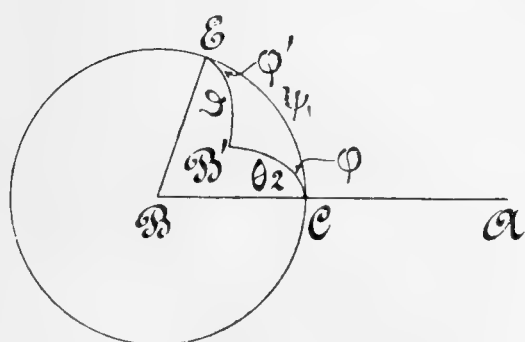


Fig. 5.

In the plane containing the line  $BA$  and the axis of the doublet at  $A$  draw an angle  $CBE = \psi$ , and introduce the angles  $EBD = \vartheta$  and  $CED = \varphi'$  as the new independent variables instead of  $\theta_2$  and  $\varphi$ <sup>1)</sup>. The integration with respect to  $\varphi'$  gives  $2\pi$ . Integration with respect to  $\vartheta$  can

also be done with ease. Let us then substitute  $g$  as independent variable instead of  $\theta_1$  and we get

$$P' = \pi \int_{\sigma}^{\tau} r^2 dr \cdot G,$$

in which

$$G = \frac{2}{c\sqrt{3}} \int_1^2 \frac{dg}{\sqrt{g^2 - 1}} (e^{cg} - e^{-cg} - 2cg),$$

<sup>1)</sup> This comes to the same thing as introducing the angle between the axis of the doublet  $B$  and the field at that point caused by the action of the doublet  $A$ . Cf. VAN DER WAALS JR. These Proceedings June 1908.

if  $c$  is here  $= \frac{hm_e^2}{r^3}$ . We can, in a way similar to that used by VAN DER WAALS JR. in solving the integral developed in his paper, evaluate  $G$  in terms of a series by expanding  $e^{cg} - e^{-cg}$  into a series of ascending powers of  $g$ . The proof of convergence can be given in the same way as by VAN DER WAALS JR.

If we write

$$v = \frac{m_e^2}{\sigma^3} \cdot \dots \cdot \dots \cdot \dots \cdot \dots \cdot \dots \quad (57)$$

for the potential energy of two molecules in contact with the axes of their doublets parallel and at the same time perpendicular to the line joining their centres and if we take as our upper limit  $\tau = \infty$  we obtain

$$B = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \left\{ 1 - \frac{1}{3!} q_1 (hv)^2 - \frac{1}{3} \frac{1}{5!} q_2 (hv)^4 - \left. \begin{array}{l} \frac{1}{5} \frac{1}{7!} q_3 (hv)^6 - \frac{1}{7} \frac{1}{9!} q_4 (hv)^8 \dots \end{array} \right\} \cdot \dots \quad (58)$$

in which

$$\begin{aligned} q_1 &= 1 + 1 \cdot \frac{1}{3} \cdot 3 &&= 2 \\ q_2 &= 1 + 2 \cdot \frac{1}{3} \cdot 3 + 1 \cdot \frac{1}{5} \cdot 3^2 &&= \frac{24}{5} \\ q_3 &= 1 + 3 \cdot \frac{1}{3} \cdot 3 + 3 \cdot \frac{1}{5} \cdot 3^2 + 1 \cdot \frac{1}{7} \cdot 3^3 &&= \frac{464}{35} \\ q_4 &= 1 + 4 \cdot \frac{1}{3} \cdot 3 + 6 \cdot \frac{1}{5} \cdot 3^2 + 4 \cdot \frac{1}{7} \cdot 3^3 + 1 \cdot \frac{1}{9} \cdot 3^4 \text{ etc} \end{aligned}$$

or

$$B = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \left\{ 1 - \frac{1}{3} (hv)^2 - \frac{1}{75} (hv)^4 - \frac{29}{55125} (hv)^6 \dots \right\}, \quad (59)$$

in which  $h$  should be replaced by  $\frac{1}{k_P T}$  if  $B$  is to be obtained as a function of  $T$ . We now obtain a series containing only the *even* powers of  $T^{-1}$  (cf. § 5).

Just as in § 5 we can now separate the terms which represent the collision virial and the attraction virial in  $B$ .

Should the law of dependence of  $B$  upon temperature for a diatomic substance in the region for which  $\gamma_{vA} = \frac{5}{2} R^1$ ) be found expe-

<sup>1)</sup> In Communication N<sup>o</sup>. 109a § 7 (March '09) the dependence of  $B$  upon temperature is given for hydrogen as deduced from the isotherms of KAMERLINGH ONNES and BRAAK. With regard to the specific heat, however, we must remark that measurements made by EUCKEN, Berlin Sitz.-Ber., Febr. 1912, p. 141, of the



rimentally to agree with that deduced from (59) one could get a fair conception of the molecule which would at least give this law of dependence upon temperature by calculating  $v$  from the temperature of the BOYLE point (if within the specified region) and  $\sigma$  from the terms in the expression for  $B$  which are independent of  $T$ , and then  $m_c$ , the moment of the doublet; from this one could, for instance, calculate the distance of the electron from the centre in the case of the molecular representation indicated at the beginning of this section. Further discussion of experimental results, however, must be postponed till a later paper.

**Physics.** — *Isotherms of monatomic substances and of their binary mixtures. XIII. The empirical reduced equation of state for argon.* By Prof. H. KAMERLINGH ONNES and Dr. C. A. CROMMELIN. Comm. N<sup>o</sup>. 128 from the physical laboratory at Leiden.

In a previous paper <sup>1)</sup> we indicated the desirability of obtaining from the mean reduced empirical equation of state for a number of normal substances which we have called VII. 1.<sup>2)</sup>, a mean reduced empirical group-equation applicable to the monatomic substances. As a first step in that direction we now give a special reduced empirical equation for argon which we shall call VII. A. 3. and which embraces data obtained from observations made in both vapour and gaseous states. <sup>3)</sup>

In previous communications similar special equations have been published, viz. one for carbon dioxide <sup>4)</sup> in gas, vapour, and liquid states, and one for hydrogen <sup>5)</sup> which embraced all available observations on the gaseous state. The important part as convenient summaries of all available experimental data played by such special

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increase of temperature undergone by a quantity of gas contained under high pressure on the addition of a measured quantity of heat showed that even at 200° K.  $\gamma_{vA}$  is for hydrogen considerably below  $\frac{5}{2}R$ , while at 60° K. the value obtained was  $\frac{3}{2}R$ . It was mentioned during the discussion at the Conseil SOLVAY, Nov. 1911, that Professor KAMERLINGH ONNES and myself had undertaken an investigation of  $\gamma_{vA}$  by KUNDT's method for hydrogen at temperatures down to that of liquid hydrogen, but this investigation has not yet been completed.

<sup>1)</sup> Proc. March 1911. Comm. N<sup>o</sup>. 120a.

<sup>2)</sup> Suppl. N<sup>o</sup>. 19 p. 18.

<sup>3)</sup> Proc. Dec. 1910, Comm. N<sup>o</sup>. 118b and C. A. CROMMELIN, Thesis for the doctorate, Leiden, 1910.

<sup>4)</sup> Arch. néerl. (2). 6. 874. 1901, Comm. N<sup>o</sup>. 74.

<sup>5)</sup> Proc. April 1909, Comm. N<sup>o</sup>. 109a.

equations in all sorts of thermodynamical calculations concerning the particular substance within the limited range through which the equation holds, makes it essential to obtain the best possible agreement between the equation and the results yielded by experiment. As the form VII. 1. was chosen for this equation with a view to its relationship to other investigations concerning the equation of state, it was fortunate that, for the comparatively small region of temperature covered by the argon observations, there were still the same number of coefficients available for the equation as had been found required to give good average agreement over the whole region covered by the equation of state for various different substances.

In the paper <sup>1)</sup> which contained the isotherm determinations for argon we have already given preliminary values for the individual virial coefficients  $A_A$ ,  $B_A$ , etc. of the equation

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v_A^2} + \frac{D_A}{v_A^3} + \frac{E_A}{v_A^4} + \frac{F_A}{v_A^5}$$

as directly calculated from the observations for each individual isotherm.

The reduced virial coefficients  $\mathfrak{B}$ ,  $\mathfrak{C}$ , etc. have now been calculated from the virial coefficients  $B_A$ ,  $C_A$ , etc. as functions of the reduced temperature  $t$ , which comes to the same as the evaluation of the constants in the equations

$$\left. \begin{aligned} \mathfrak{B} &= b_1 t + b_2 + \frac{b_3}{t} + \frac{b_4}{t^2} + \frac{b_5}{t^3} \\ \mathfrak{C} &= c_1 t + c_2 + \frac{c_3}{t} + \frac{c_4}{t^2} + \frac{c_5}{t^3} \end{aligned} \right\} \text{etc.} \quad (I)$$

By this the coefficients are adjusted to the observations with respect to both temperature and density.

We may here give a short résumé of the manner in which these calculations were carried out.

As in the present instance the final terms of the polynomial  $pv_A = A_A + \frac{B_A}{v_A} + \text{etc.}$  exert but a slight influence and therefore can be calculated only approximately from the observations, it was

<sup>1)</sup> Proc. Dec. 1910. Comm. N<sup>o</sup>. 118b and C. A. CROMMELIN, Thesis for the doctorate, Leiden 1910.

<sup>2)</sup> Proc. June 1901, Comm. N<sup>o</sup>. 71 and Arch. néerl. (2) 6. 874 1901, Comm. N<sup>o</sup>. 74.

As can be seen a 5th term has been added to the equations there given. For the formulae connecting  $B_A$  and  $\mathfrak{B}$ ,  $C_A$  and  $\mathfrak{C}$ , etc., reference may be made to the former paper. In the present paper we shall use chiefly the reduced virial coefficients which are to be preferred for the adjustment of the values of the coefficients.

best to begin with the adjustment of these terms. The fairly great changes which these terms as a rule undergo, have but a slight influence upon the values of the initial coefficients, while, on the other hand, small changes made in the initial coefficients in the process of adjustment occasion appreciable alterations in the coefficients of the final terms, and so the adjustment of the values of the final coefficients would become more difficult than it is as a rule at small densities.

In the case of argon the coefficients  $\mathfrak{E}$  and  $\mathfrak{F}$  need not be taken into account, for their values have been adopted from VII. 1. <sup>1)</sup> and consequently they have already been adjusted to the observations. Our calculations therefore began with the adjustment of  $\mathfrak{D}$ , which, as a glance at the values of  $D_A$  already published <sup>2)</sup> will clearly show, had to be done in a somewhat arbitrary manner. Some of these  $D_A$ 's have been taken from VII. 1. The values of  $D_A$  at the lower temperatures, which were very irregular, were now plotted, while for  $t = 6$  the  $D_A$  value from VII. 1 was included. In this way values of  $D_A$  or  $\mathfrak{D}$  were graphically smoothed, and then the deviations of these smoothed values from VII. 1. were represented as functions of the reduced temperature by a linear equation

$$\Delta\mathfrak{D} = \Delta\delta_1 t + \Delta\delta_2$$

(in which

$$\Delta\mathfrak{D} = \mathfrak{D}_a - \mathfrak{D}_{\text{VII.1.}}$$

$$\Delta\delta_1 = \delta_{1,a} - \delta_{1,\text{VII.1.}}$$

$$\Delta\delta_2 = \delta_{2,a} - \delta_{2,\text{VII.1.}}$$

In this way  $\delta_{1,a}$  and  $\delta_{2,a}$  were calculated as functions of the reduced temperature, while  $\delta_{3,a}$ ,  $\delta_{4,a}$  and  $\delta_{5,a}$  were taken from VII.1.

The values of  $\mathfrak{D}$  adjusted in this way were then converted into  $D_A$  and were used in the first place to get an idea of the magnitude of the corrections to be applied to the values of  $\mathfrak{B}$  and  $\mathfrak{C}$  so as to give the best possible agreement with the observations. When this was done we could then proceed to the adjustment proper of the values of  $B_A$  and  $C_A$ , or rather of  $\mathfrak{B}$  and  $\mathfrak{C}$  according to the formulae (I).

As can be seen from what follows, this process yielded values of the coefficients which, especially as regards the  $\mathfrak{B}$  coefficient, did not differ much from those of VII.1. while, at the same time, a comparison with the experimental data of the reduced equation of state

<sup>1)</sup> Suppl. N<sup>o</sup>. 19 p. 18.

<sup>2)</sup> Proc. Dec. 1910, Comm. N<sup>o</sup>. 118b.

thus obtained gave thoroughly satisfactory results. The results of all these calculations viz. the coefficients  $b_1, b_2, b_3, b_4, b_5, c_1, c_2$  etc., of the equation VII. A. 3., the virial coefficients obtained from these, and finally, the comparison of VII. A. 3. with the experimental data are given in the following tables.

The figures italicised in the tables are those which have been taken from VII. I.

TABLE I. Coefficients of the equation VIII. A. 3.

	1	2	3	4	5
$b \times 10^3$	+ 137.193	- 146.732	- 505.734	+ 94.358	- 17.8488
$c \times 10^{11}$	+ 97.9740	- 528.608	+ 836.166	- 315.182	+ 77.4006
$d \times 10^{18}$	+ 236.30	+ 421.825	- 903.004	+ 367.7055	- 178.5625
$e \times 10^{25}$	- 1588.948	+ 5725.652	- 4331.720	+ 864.610	+ 40.449
$f \times 10^{32}$	+ 1685.000	- 6477.876	+ 6019.629	- 1512.028	+ 144.537

TABLE II. Virial coefficients of equation VII. A. 3.

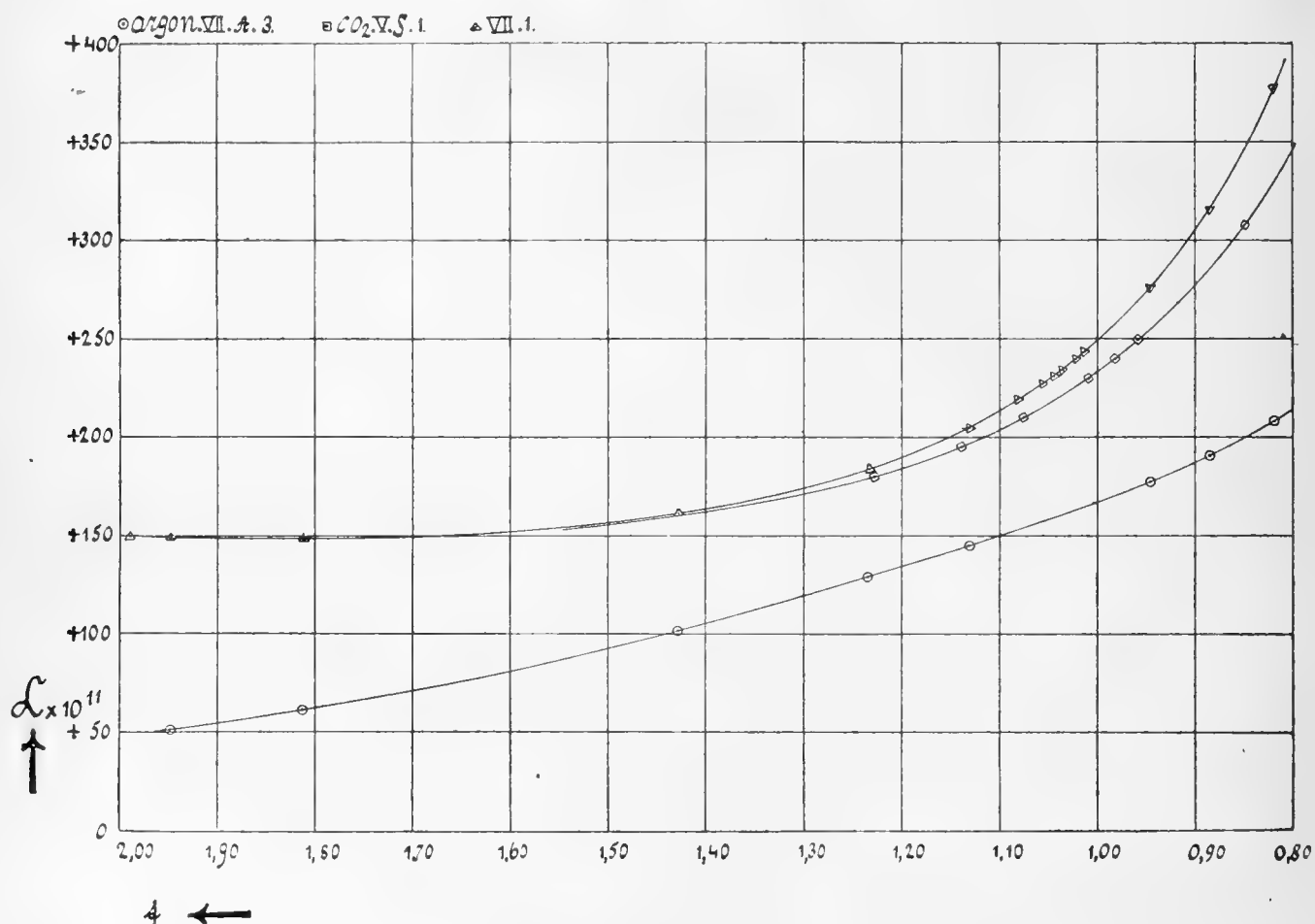
$s$	$A_A$	$B_A \times 10^3$	$C_A \times 10^6$	$D_A \times 10^{12}$	$E_A \times 10^{18}$	$F_A \times 10^{24}$
+ 20.39	+ 1.07545	- 0.60178	+ 0.76768	+ 6.78079	+ 7.6045	- 4.35430
0.00	+ 1.00074	- 0.76763	+ 0.91203	+ 5.93894	+ 8.7321	- 4.98937
- 57.72	+ 0.78922	- 1.30257	+ 1.50907	+ 3.28679	+ 10.5255	- 5.02409
- 87.05	+ 0.68174	- 1.62411	+ 1.92013	+ 1.18908	+ 10.5566	- 3.93044
- 102.51	+ 0.62511	- 1.81201	+ 2.16108	+ 0.72267	+ 10.4013	- 3.10842
- 109.88	+ 0.59810	- 1.90692	+ 2.28115	+ 0.20350	+ 10.3251	- 2.69045
- 113.80	+ 0.58372	- 1.95896	+ 2.34653	- 0.09396	+ 10.2947	- 2.47655
- 115.86	+ 0.57617	- 1.98675	+ 2.38134	- 0.25708	+ 10.2837	- 2.35600
- 116.62	+ 0.57340	- 1.99711	+ 2.39431	- 0.31873	+ 10.2806	- 2.31432
- 119.20	+ 0.56393	- 2.03255	+ 2.43867	- 0.53362	+ 10.2759	- 2.17669
- 120.24	+ 0.56012	- 2.04701	+ 2.45677	- 0.62312	+ 10.2764	- 2.12239
- 121.21	+ 0.55658	- 2.06056	+ 2.47376	- 0.70808	+ 10.2783	- 2.07246
- 130.38	+ 0.52296	- 2.19283	+ 2.64178	- 2.10863	+ 10.3966	- 1.66293
- 139.62	+ 0.48909	- 2.33484	+ 2.83477	- 2.41358	+ 10.8045	- 1.42979
- 149.60	+ 0.45252	- 2.50118	+ 3.10431	- 2.78849	+ 11.8440	- 1.53961

TABLE III. Comparison of equation VII. A. 3 with observation.

$d_A$	O-C in %	$d_A$	O-C in %	$d_A$	O-C in %	$d_A$	O-C in %
+ 20°.39		0°.00		- 57°.72		- 87°.05	
20.499	- 0.07	21.877	+ 0.05	23.509	+ 0.11	25.152	+ 0.17
25.759	+ 0.01	26.581	- 0.02	[28.575	- 0.16]	34.467	+ 0.02
32.590	+ 0.14	32.302	+ 0.05	33.793	- 0.05	55.822	- 0.10
35.330	- 0.09	37.782	- 0.06	48.116	0.00	71.444	- 0.06
35.759	- 0.13	51.840	- 0.15	64.948	+ 0.06	94.625	- 0.14
47.319	- 0.04	65.325	- 0.21	90.695	+ 0.11	119.84	+ 0.19
59.134	+ 0.07						
59.250	- 0.06						
- 102°.51		- 109°.88		- 113°.80		- 115°.86	
25.571	+ 0.19	26.242	+ 0.14	67.078	- 0.16	69.947	- 0.23
35.077	0.00	34.807	+ 0.26	88.889	- 0.13	91.308	- 0.18
[47.893	+ 0.47]	65.142	- 0.54	106.68	- 0.34	108.02	- 0.35
[53.752	+ 0.48]	66.530	- 0.29	129.17	- 0.25	131.51	- 0.38
62.240	- 0.05	87.176	+ 0.01	152.71	- 0.14	155.12	- 0.27
[69.954	+ 0.50]	102.76	- 0.20	155.40	- 0.07	179.94	- 0.06
84.002	- 0.08	125.56	- 0.09	182.13	+ 0.37	[183.35	+ 2.40]
95.802	- 0.17	148.32	+ 0.03	184.82	+ 0.27	235.47	+ 1.16
115.88	- 0.17	152.79	- 0.26	212.99	+ 1.02	319.52	+ 0.20
135.65	- 0.01	180.84	+ 0.37				
158.01	+ 0.13						
- 116°.62		- 119°.20		- 120°.24		- 121°.21	
26.480	+ 0.25	26.871	+ 0.24	72.627	- 0.04	27.326	+ 0.24
34.939	- 0.01	34.965	+ 0.24	82.816	+ 0.10	35.283	+ 0.25
68.630	- 0.13	[70.314	- 0.25]	99.246	+ 0.03	71.459	- 0.10
90.563	- 0.21	70.481	- 0.66	118.51	- 0.10	85.580	- 0.05
110.19	- 0.46	70.580	- 0.56	136.31	- 0.02	100.33	- 0.03
133.69	- 0.39	83.257	- 0.63	165.79	- 0.09	[123.85	- 0.19]
159.71	- 0.25	96.834	- 0.31	206.57	+ 0.82	148.95	- 0.10
161.75	- 0.35	98.863	- 0.83	280.25	+ 3.22	170.05	- 0.16
[186.15	+ 0.13]	124.97	- 1.10	338.95	+ 0.89	234.13	+ 1.73
210.02	+ 0.64	[143.71	- 0.44]			333.75	+ 1.93
[260.61	+ 1.74]	156.36	- 1.07				
331.29	- 0.46	[172.25	+ 0.07]				
		222.69	- 0.04				
		275.02	+ 1.11				
		336.89	- 1.72				
- 130°.38		- 139°.62		- 149°.60			
27.394	+ 0.30	28.122	+ 0.12	29.183	- 0.03		
[31.583	- 0.44]	35.573	- 0.10	34.646	- 0.14		
34.726	+ 0.24						
55.807	+ 0.20						
65.125	+ 0.14						
77.821	+ 0.77						
[101.71	- 0.81]						

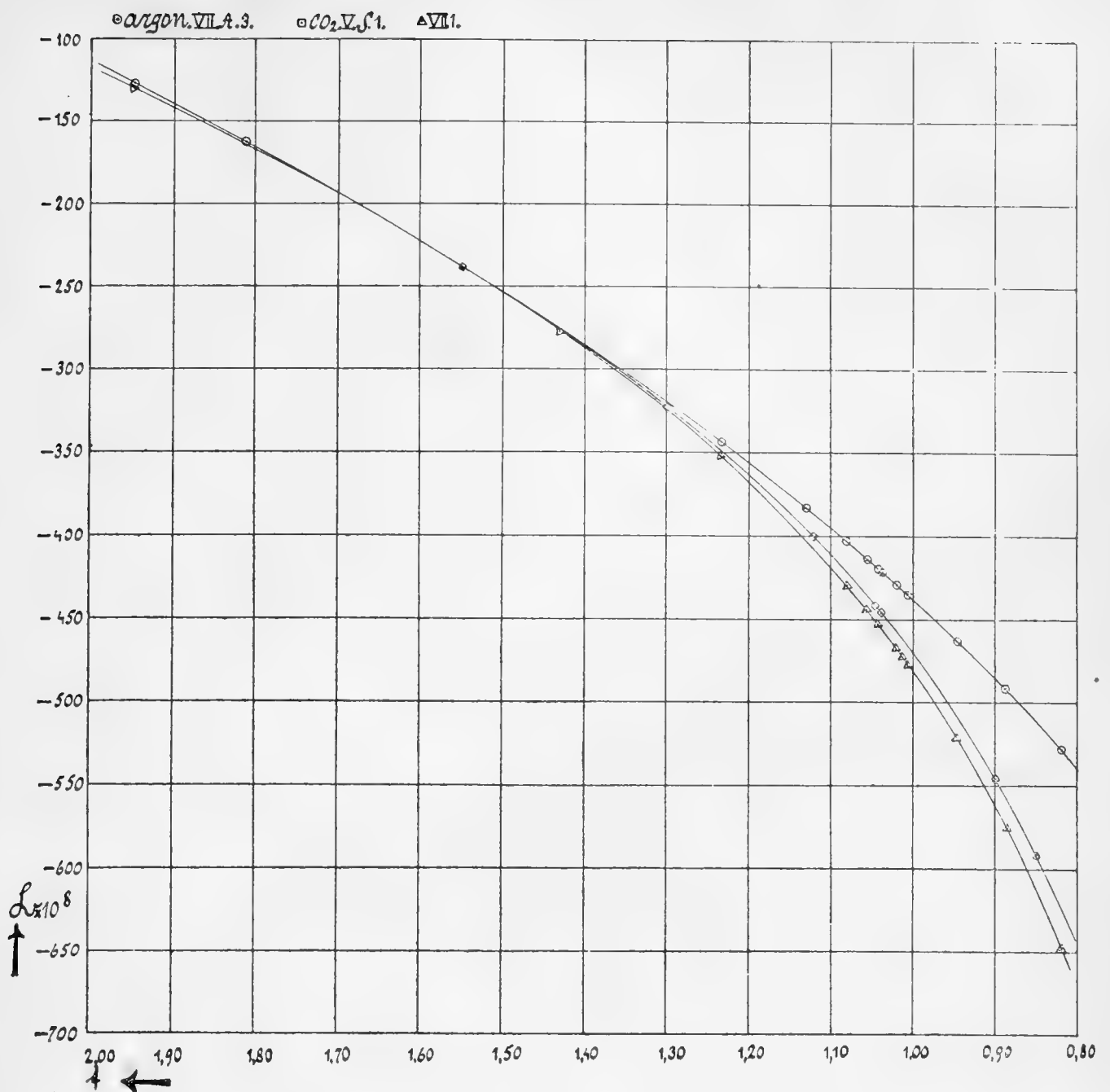
The accompanying diagrams exhibit the reduced coefficients  $\mathfrak{B}$  and  $\mathfrak{C}$  as functions of the reduced temperature  $t$  within the region of observation for argon, that is, from  $t = 2$ , to  $t = 0.8$ . The curves drawn through the circles refer to the special argon equation VII. A. 3, those through the triangles to the mean reduced equation VII. 1. and those through the squares to the special equation for carbon dioxide, V. S. 1. <sup>1)</sup>

As the experimental data at present employed are very limited in scope we must, in the meantime, be somewhat chary of drawing conclusions as to the mutual actions of molecules when they come within each other's immediate neighbourhood from a comparison of VII. A. 3. with the equations for the other substances shown in our diagrams. In the case of the  $\mathfrak{B}$  coefficient the absence of data at small values of  $t$  is specially felt <sup>2)</sup>, while as far as  $\mathfrak{C}$  and the special argon equation are concerned it is the absence of data towards the side of high densities. Equation VII. A. 3 can, therefore, be regarded only as a first step towards the formation of *the* empirical equation of state for argon.



<sup>1)</sup> Arch. Néerl. (2), 6, p. 874, 1901. Comm. N<sup>o</sup>. 74.

<sup>2)</sup> We hope to be able to publish shortly some experimental results to supply this deficiency.



We may still take it, however, that we have advanced a step since our previous papers<sup>1)</sup>. It was there found that deviations of the isotherms in the gas state were systematically connected with deviations of the diameter and of the vapour pressure curves (with which the deviations of the latent heat of vaporization etc., are connected by thermodynamical formulae), while in the present case a much simpler survey is obtained of the deviations of the isotherms at densities at which the virial coefficient  $D$  need not be taken into account. These are shown in the two curves for  $\mathfrak{B}$  and  $\mathfrak{C}$ , which therefore play pretty much the same part in this particular region as the boundary curve for equilibrium between liquid and vapour. And it is again striking how the various substances arrange them-

<sup>1)</sup> Proc. March 1911, Comm. N<sup>o</sup>. 120b and Proc. July 1911, Comm. N<sup>o</sup>. 121b.

selves as far as these deviations are concerned according to the more or less complicated structure of their molecules. The curves for VII. 1 in the region of reduced temperature to which the diagrams refer are obtained chiefly from isopentane and ether, substances which have very complex molecules; after these come, in the order given, carbon dioxide, with an undoubtedly less complex molecule, and finally argon. Clearly, just as was the case with the deviations which were encountered in a previous paper<sup>1)</sup>, one must look for the explanation of this in a real or apparent compressibility which diminishes in magnitude as the molecule becomes less complex in shape or structure, or in a characteristic behaviour of the attraction potential determined by this peculiarity.

We hope to present further communications shortly giving results of calculations of various thermodynamical quantities which may be made from the equation now given within the limited region for which it holds.

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<sup>1)</sup> Proc. July 1911. Comm. N<sup>o</sup>. 121*b*.



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING  
of Saturday September 28, 1912.

*President:* Prof. H. A. LORENTZ.

*Secretary:* Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 28 September 1912, Dl. XXI).

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**Physiology.** — “*Comparative researches on young and old erythrocytes.*”<sup>1)</sup> By J. SNAPPER. (Communicated by Prof. H. J. HAMBURGER.)

(Communicated in the meeting of June 29, 1912).

### 1. *Introduction.*

Of late years various investigations have been carried out with a view to ascertain if there are differences between newly formed red blood-corpuscles and those which have already circulated for some time. For this purpose the blood was examined of animals which had been made anaemic in some way or other. Since the loss of blood must be made up for by fresh red blood-corpuscles, we may depend upon it that the differences existing between the blood before and after the artificial anaemia was effected, are caused by the new formation of fresh red blood-corpuscles.

According to recent<sup>2)</sup> investigations there is a difference between new red corpuscles, formed after bleeding, and those formed after blood has been lost by injections with blood poisons. This difference manifested itself especially when the capacity of resistance of the blood-corpuscles was tested by means of hypotonic salt-solutions. Whilst the blood-corpuscles of an animal which had been made anaemic by poison-injections resisted the hypotonic salt-solution better than the blood-corpuscles of a normal animal, this was said not to be the case with those animals of which the anaemia had been caused by bleeding.

There are indeed reasons to assume that the regeneration after poison-injections will be stronger than after bleedings. Yet it is improbable that the young red blood-corpuscles formed after bleeding, should not be distinguished in the same way from the old erythrocytes — though it may be in a slighter degree — as those formed after poison-injections. These slighter differences too, may be of importance, however. As we know, the anaemia effected by injections of poison causes the number of blood-corpuscles to decrease so strongly that sometimes only 16 % of the original number are left. It is not improbable that after such an extreme loss of blood the regeneration may be an abnormal one. On the other hand the properties of new red blood-corpuscles, formed after a smaller loss of blood will bear a greater resemblance to the properties of young red blood-corpuscles formed under physiological conditions.

<sup>1)</sup> A more detailed account of these investigations will be published elsewhere.

<sup>2)</sup> ITAMI and PRATT, *Biochem. Zeitschrift*, Bd. 18.

SÄTTLER, *Folia Haemat*, 1910.

In order to discover these minuter differences it was necessary to subtilize the method. For this purpose the following considerations were held in view. In the experiments mentioned above only the maximum and minimum capacity of resistance of the young erythrocytes had been determined.

The determination of this capacity is, as is generally known, based on the following facts.

When red blood-corpuscles are suspended in a salt-solution with an osmotic pressure less than 0,9 % NaCl, they absorb water which causes them to swell. The lower the osmotic pressure of the salt-solution, the more water they will absorb. At last they burst and the haemoglobin, contained in them, enters the solution. The lower the osmotic pressure of the medium in which they can only just maintain themselves, the greater the capacity of resistance of the red blood-corpuscles. Seeing that not all the blood-corpuscles have the same capacity of resistance the *minimum* capacity of resistance of the blood is expressed by the most concentrated Na Cl-solution which already causes haemolysis. In this solution the weakest blood-corpuscles lose their haemoglobin. The *maximum capacity of resistance* of the blood is determined by the Na Cl-solution in which the haemolysis is complete, and which cannot be resisted even by the strongest blood-corpuscles. *Only these two salt-solutions have been determined in the above-mentioned investigations: as to the degree of haemolysis caused by the intermediate solutions every detail is wanting.*

By determining this degree we succeeded in discovering some qualities by which blood-corpuscles, newly formed after blood has been lost, are distinguished from the other, remaining ones. It was also found possible to study the mechanism of the regeneration more closely. The experimental method may be described as follows.

## 2. *Experimental method.*

The blood experimented upon was always that of rabbits. It was obtained by a slight cut in the ear and defibrinated by being beaten with 2 glass rods. A series of centrifugating tubes was filled with 5 cm<sup>3</sup> NaCl-solution in progressive concentrations, the difference between two successive concentrations being 0.02 %. To these 5 cm<sup>3</sup> 0.1 cm<sup>3</sup> of blood was added and the mixture was shaken thoroughly. Then the solutions were left exposed to the temperature of the room for a few hours; subsequently they were centrifugated. In the tube where red blood-corpuscles no longer settle at the bottom, the haemolysis is complete. In the other tubes, where blood-corpuscles have

remained intact, less haemoglobin has been dissolved. *The degree of haemolysis in these tubes is expressed by the proportion between the haemoglobin concentration in these tubes and the haemoglobin concentration of the tube with complete haemolysis.* These proportions can be easily calculated by making use of the colorimetric method first suggested by ARRHENIUS<sup>1)</sup>. Thus a series of values is obtained expressing which percentage of the complete haemolysis is caused by each salt-concentration. (Table A). The progress of this haemolysis may be expressed by a curve, the absciss of which is formed by the NaCl-concentrations and the ordinate by the degrees of haemolysis effected by each concentration. (Fig. 1).

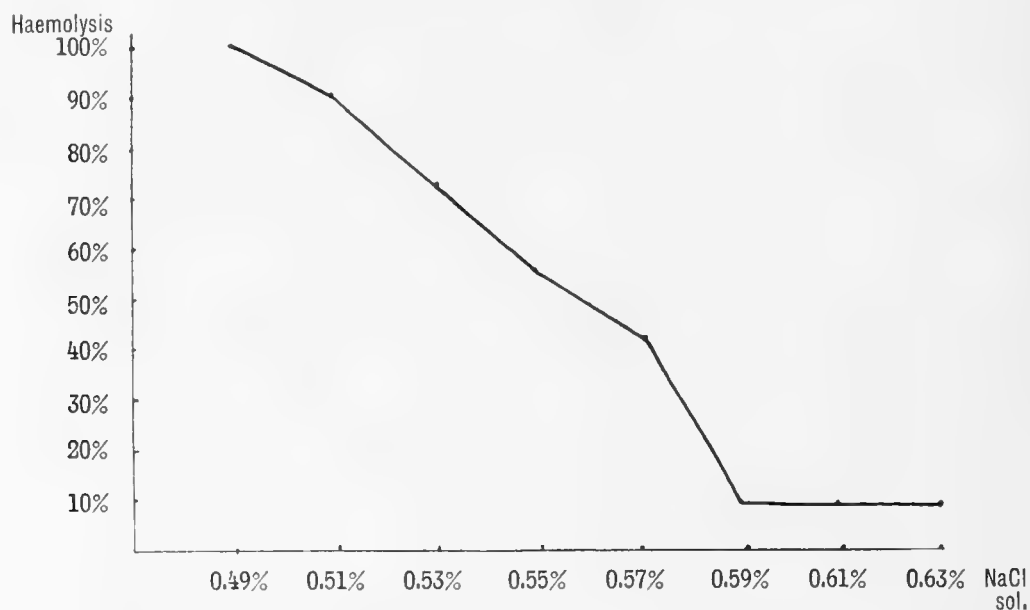


Fig. 1. Graphical representation of Table A.

TABLE A. Denoting the haemolysis caused by each NaCl concentration.

0.63 % NaCl solution caused	9 % haemolysis
0.61 » » » »	9 » »
0.59 » » » »	9 » »
0.57 » » » »	42 » »
0.55 » » » »	55 » »
0.53 » » » »	73 » »
0.51 » » » »	91 » »
0.49 » » » »	100 » »

### 3. *The capacity of resistance of old and new erythrocytes against diluted salt-solutions.*

The blood of an animal which has been made anaemic by bleeding, may be examined in the same way as that of a normal animal.

<sup>1)</sup> ARRHENIUS and MADSEN, Zeitschr. für Physikal. Chemie 1903.

After every bleeding the degree of haemolysis, caused by the different salt-solutions, is determined. (Table B). When we also represent these values graphically, the curve after every venesection is found to have moved in the direction of the lower concentrations. (Fig. 2). In the normal animal 80% is set free at a concentration of 0.49% NaCl. After one venesection the same solution causes 66% of haemolysis and after 2 venesections only 25%. In other words whilst only 20% of the blood-corpuses of the normal animal could resist a NaCl-solution of 0.49%, the composition of the blood is changed to such an extent after two venesections, that 75% of the blood corpuscles can still bear this concentration. Moreover, the haemolysis was complete in the case of the normal animal at 0.47% NaCl. After two bleedings the same 0.47% NaCl solution caused an haemolysis of 40% only. Hence there were in the blood of the anaemic animal  $100\% - 40\% = 60\%$  blood corpuscles which could withstand a less concentrated salt-solution than the most resistant blood-corpuses of the normal animal. These 60% are, therefore, blood corpuscles which were not met with in the non-anaemic animal. They have been newly formed after the bleeding; they are the new blood-corpuses which are to replace the lost ones. *Also the young blood-corpuses, formed after a venesection, have an increased capacity of resistance*<sup>1)</sup>.

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<sup>1)</sup> About the quantity of haemoglobin new erythrocytes contain, more particulars might be discovered by counting the number of erythrocytes which remain in every concentration. If we compare this with the quantity of haemoglobin set free, then it may be decided whether the old erythrocytes contain more or less haemoglobin than the new ones. If for instance the old, that is to say the blood corpuscles with smaller resistance contained more haemoglobin, then in the more concentrated solutions more haemoglobin would proportionately be set free than in the less concentrated ones. Generally speaking, however, the values are found to agree very well.

It is impossible to settle this question conclusively, the method of counting, as suggested by ZEISS-THOMA, allowing of no closer determination than with an error of 5%. This causes deviations in the agreement of the values.

By means of the haematokrit-method it can be determined whether there are any differences between the volumes of old and new erythrocytes. For this purpose the volume of the cells, left after each concentration, was compared with the number of erythrocytes left. Though here too, the values were found to agree, the method employed in counting gave rise again to important inaccuracies.

Besides, an equal average volume of new and old blood-corpuses would be the more remarkable since according to unpublished investigations of this institute made by HAMBURGER and KOOY, the diameter of new blood corpuscles is greater than that of old ones.

It would follow from this that new and old erythrocytes differ in shape.

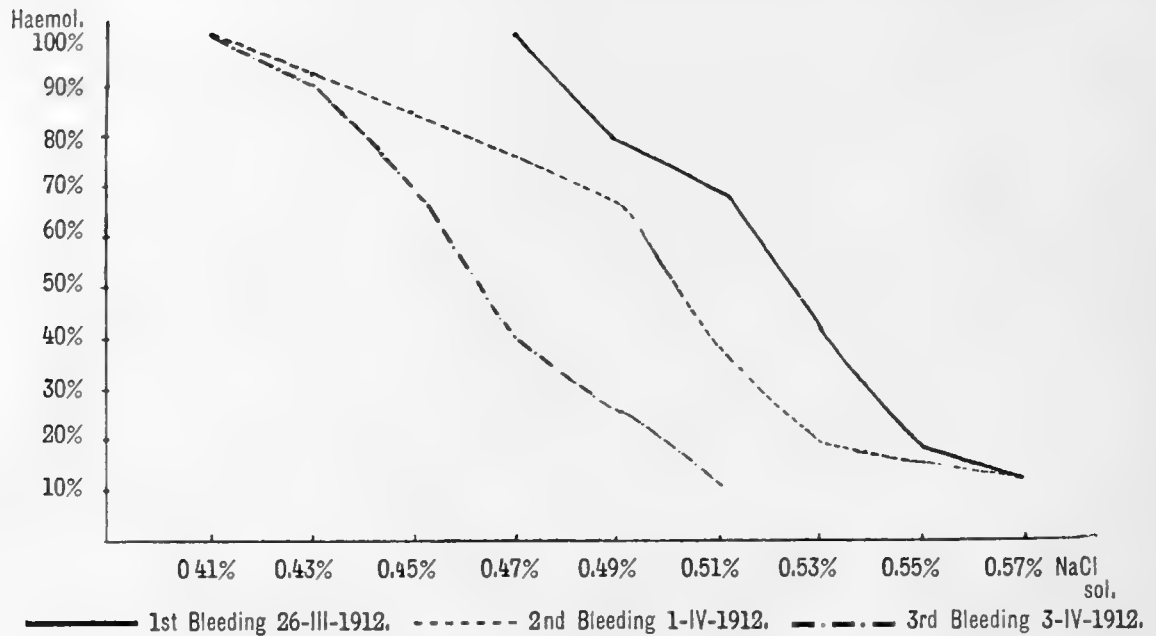


Fig. 2. graphical representation of Table B.

TABLE B, denoting the haemolysis caused by each NaCl-concentration in the normal and the anaemic animal.

	1st Venesection	2nd Venesection	3rd Venesection	
At 0.57 pCt. NaCl	12 pCt.	12 pCt.	—	} Haemoglobin was found in the solution
" 0.55 " "	18 "	15 "	—	
" 0.53 " "	42 "	19 "	—	
" 0.51 " "	67 "	37 "	10 pCt.	
" 0.49 " "	80 "	66 "	25 "	
" 0.47 " "	100 "	75 "	40 "	
" 0.45 " "	—	84 "	67 "	
" 0.43 " "	—	91 "	90 "	
" 0.41 " "	—	100 "	100 "	

#### 4. *New erythrocytes are built up from old ones.*

The values and curves of fig. 2 may also be viewed in another way. On the first day, for instance, a solution of 0.57 % NaCl causes 12 % haemolysis, whilst at 0.55 % NaCl 18 % of the erythrocytes had disappeared. Hence there were then  $18\% - 12\% = 6\%$  blood-corpuses which were just unable to withstand a solution of 0.55 % NaCl. For 6 % of the blood corpuses 0.55 % NaCl is just the minimum concentration they can bear.

TABLE C. Same rabbit as Fig. 2 and Table B.

	1st Venesection	2nd Venesection	3rd Venesection
Whilst they can still bear a slightly stronger concentration they burst at 0.57 pCt. NaCl	12 pCt.	12 pCt.	—
" " " " " " " " " " " "	6 "	3 "	—
" " " " " " " " " " " "	24 "	4 "	—
" " " " " " " " " " " "	25 "	18 "	10 pCt.
" " " " " " " " " " " "	13 "	29 "	15 "
" " " " " " " " " " " "	20 "	9 "	15 "
" " " " " " " " " " " "	—	9 "	27 "
" " " " " " " " " " " "	—	7 "	23 "
" " " " " " " " " " " "	—	9 "	10

Thus it can be established for every concentration, which percentage of the bloodcorpuscles lose their haemoglobin in one particular solution, whilst they could withstand a solution which was 0.02 % stronger.

If, therefore, we analyse in this manner the values obtained with the anaemic animal every day, then we shall find for which percentage of the erythrocytes every salt-solution represents the minimum concentration. (See Table C). The 3 series of values obtained, may be expressed again in curves (Fig. 3). There are always one or two salt-concentrations representing for the greater number of erythrocytes the minimum concentration they can bear. On the first day these maxima are found at 0.53 % and 0.51 % NaCl, on the second day at 0.49 % NaCl, and on the third day at 0.45 % and 0.43 % NaCl.

These maxima too move in the direction of the less concentrated solutions.

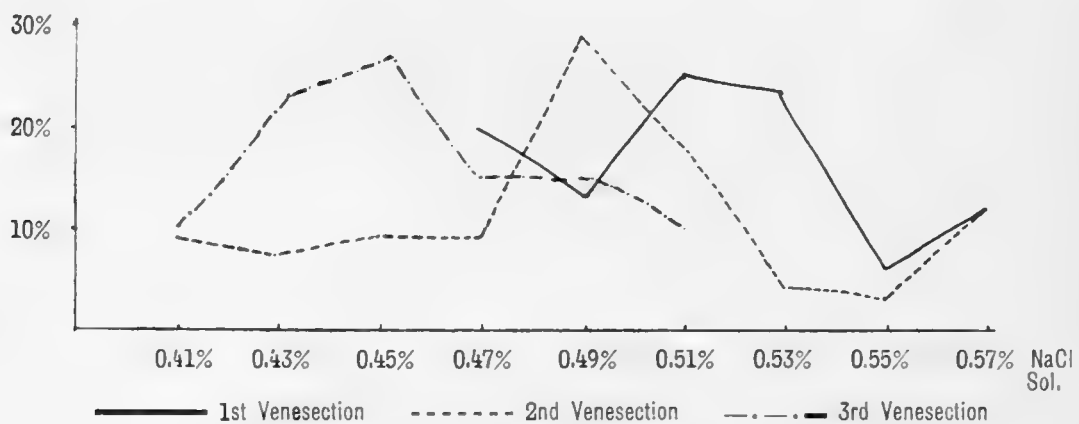


Fig. 3. Graphical representation of Table C.

It follows from this

	2nd Venesection	3rd Venesection
Bloodcorpuscles bursting just at 0.55 pCt. NaCl	equal	decreased
" " " " 0.53 " "	decreased	"
" " " " 0.51 " "	"	"
" " " " 0.49 " "	increased	"
" " " " 0.47 " "	decreased	increased
" " " " 0.45 " "	newly formed	"
" " " " 0.43 " "	"	"
" " " " 0.41 " "	"	equal

Hence the number of strong blood-corpuscles increases as the number of weak ones decreases. This increase on the one hand and



decrease on the other, run so exactly parallel, that we are at once tempted to trace a connection between them.

Moreover the weaker ones are found to decrease much more strongly than can be explained by mere loss of blood only. If no regeneration were to take place, the proportion between the weaker and the stronger blood-corpuscles would not be modified at all. At the regeneration, therefore, the number of weaker bloodcorpuscles must become relatively smaller since it is just the new bloodcorpuscles which have a great capacity of resistance. Even if the entire loss of blood had been made up for, this strong decrease of the weaker ones cannot be explained. The rabbit weighed 2000 grammes, contained, therefore,  $\frac{8}{100} \times 2000 = 160$  gr. of blood. After 2 bleedings of 15 ccM. (that is about 20 % of the whole) of the 80 % erythrocytes which are destroyed at 0.49 % NaCl only 25 % are found back. These weaker bloodcorpuscles decrease, therefore, much more strongly than can be explained by loss of blood only: they must be used in some way or other. Since, moreover, the increase of the stronger bloodcorpuscles runs parallel to the decrease of the weaker ones, we may with a great amount of probability assume that the *young red bloodcorpuscles are built up out of the weaker ones.*

Now it can also be explained why the young blood corpuscles develop a greater capacity of resistance as more blood is withdrawn. The weaker bloodcorpuscles decreasing very strongly after every bleeding, the old bloodcorpuscles, which in the anaemic animal serve to build up the new ones, are already much stronger than the old bloodcorpuscles which are disintegrated in the normal animal for this purpose. As the material out of which they are built up grows stronger and stronger, the young blood-corpuscles are stronger too after each venesection.

*This also supplies us with one of the chief causes of the difference between erythrocytes, formed after bleeding, and those formed after poison-injections.*

Owing to the abnormally strong decrease of the number of bloodcorpuscles after poison-injections, the newly formed cells could not but become very strong — much stronger than after a few bleedings.

5. *Also in the blood the regeneration greatly surpasses the loss.*

Finally a conclusion may be arrived at as regards the degree of the regeneration. After 2 venesections about 20 % of the blood of the rabbit had been withdrawn. At the third bleeding 60 % bloodcorpuscles were found with a greater capacity of resistance

than the strongest of the normal animal. After 20% blood has been withdrawn at least 60% new cells are formed. In this case too, the rule of WEIGERT, applicable in general pathology, holds good: *the regeneration surpasses the loss by far*. Only with regard to blood it cannot be deduced from the number of bloodcorpuscles, because for each new bloodcorpuscle an old one has to be disintegrated. Hence the absolute number of bloodcorpuscles per m.M<sup>3</sup>. can increase but slowly.

Yet this strong regeneration of the blood-corpuscles too, has probable a beneficial effect upon the organism. Though there is no difference as regards size or haemoglobin-percentage, MORAWITZ has pointed out the fact that while blood in normal circumstances can bind chemically hardly any oxygen, the anaemic blood consumes rather large quantities of O<sub>2</sub><sup>1)</sup>. Hence the new blood-corpuscles differ qualitatively from the old ones, which appears besides from their increased capacity of resistance.

#### 6. *Effect of the serum on haemolysis.*

##### a. *The serum is replaced by 0.9% NaCl.*

Before drawing the conclusions, mentioned above, *it was necessary to determine the effect which the serum has upon haemolysis*. Mostly we read that the serum contains substances which impede haemolysis<sup>2)</sup>, for when the blood-corpuscles have been washed with 0.9% NaCl-solution, their capacity of resistance has decreased. If these substances were really present, it might have a considerable effect upon the capacity of resistance of anaemic blood. In anaemic blood there is relatively more serum than in normal blood: the greater quantity of serum would impede haemolysis more strongly, and this might give an impression of a greater capacity of resistance.

It is indeed found that *the capacity of resistance of the blood is lessened when it is washed with 0.9% NaCl*. (See Fig. 4).

##### b. *The serum is replaced by 4% glucose.*

That this is not due, however, to the effect of the serum having disappeared, but probably to osmotic changes, follows from the fact that washing with an isotonic glucose solution (4%) does not modify the capacity of resistance (See Fig. 4).

<sup>1)</sup> MORAWITZ, Archiv f. exper. Pathol. u. Pharmacol. Bd 60.

<sup>2)</sup> GROS. Ztschr. f. exper. Pathol. u. Pharmacol. Bd. 62.

SATTLER l.c.

Seeing that glucose cannot enter the blood-corpuses, no ions can leave them. A solution leaving intact the osmotic equilibrium does not modify the capacity of resistance. Hence the removal of the serum by washing the blood-corpuses need not alter the capacity of resistance.

*The serum contains, therefore, no substances which impede haemolysis.*

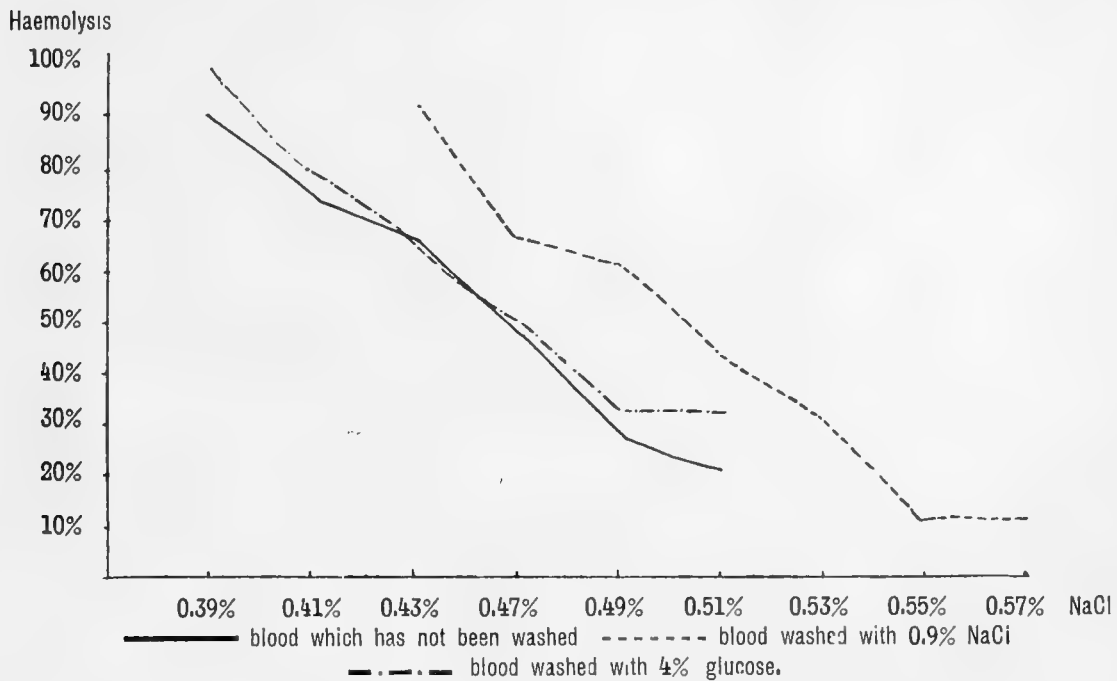


Fig. 4. Graphical representation of Table D.

TABLE D. When the blood has been washed with 0.9 pCt. NaCl-solution, the same NaCl-concentration effects more haemolysis than it does in blood which has not been washed.

Blood, washed with a 4 pCt. glucose-solution has *no* decreased capacity of resistance.

	Blood which had not been washed	Blood washed with 0.9 pCt. NaCl	Blood washed with 4pCt. glucose	
At 0.57 pCt. NaCl	—	11 pCt.	—	Haemoglobin had been set free
" 0.55 " "	—	11 "	—	
" 0.53 " "	—	31 "	—	
" 0.51 " "	21 pCt.	44 "	33 pCt	
" 0.49 " "	27 "	61 "	33 "	
" 0.47 " "	47 "	66 "	50 "	
" 0.45 " "	66 "	92 "	66 "	
" 0.43 " "	73 "	—	80 "	
" 0.41 " "	91 "	—	100 "	

7. In the osmotic disturbance, caused by washing with 0.9 % NaCl, the ions of Ca play a prominent part.

This disturbance of the osmotic equilibrium of the blood-corpuscles, caused by washing with 0.9 % NaCl, is not effected if we wash with 0.9 % NaCl + 0.1 % CaCl<sub>2</sub>. What was pointed out before in the case of leucocytes, viz. the importance of ions of Ca<sup>1)</sup>, is also found to apply to the erythrocytes. Though only traces of Ca are found in the erythrocytes, yet their capacity of resistance is considerably modified if osmose causes these few ions to disappear.

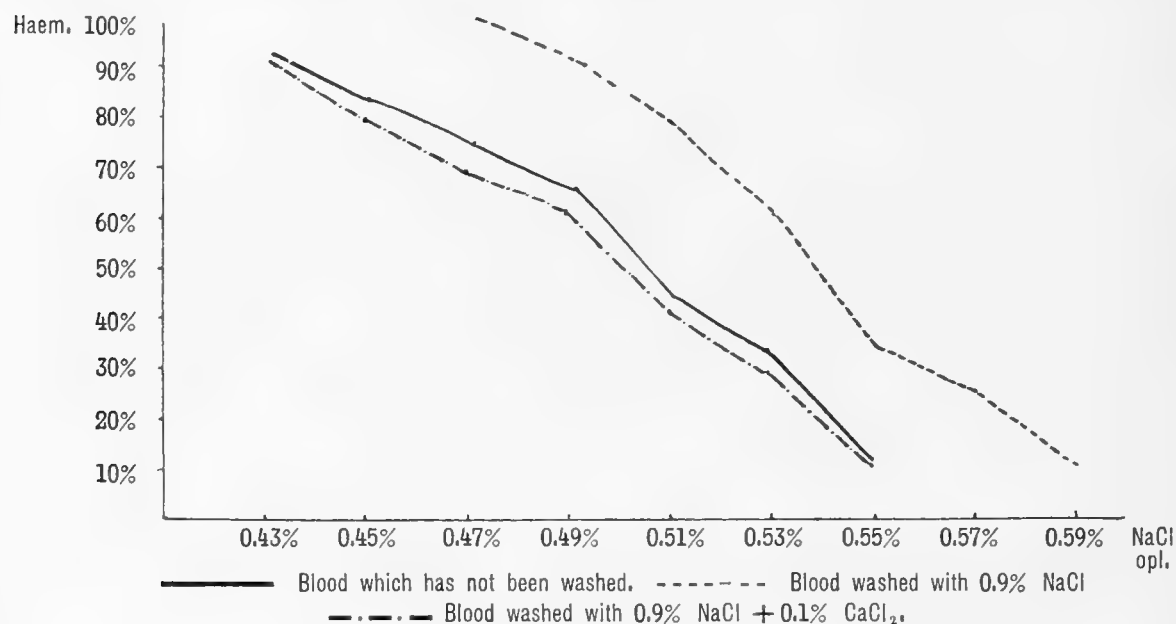


Fig. 5. Graphical representation of Table E.

TABLE E. Blood which has been washed with a 0.9 pCt. NaCl-solution has a decreased capacity of resistance.

Blood which has been washed with a 0.9 pCt. NaCl + 0.1 pCt. CaCl<sub>2</sub>-solution has *no* decreased capacity of resistance.

	Blood which had not been washed	Blood washed with 0.9 pCt. NaCl	Blood washed with 0.9 pCt. NaCl + 0.1 pCt. CaCl <sub>2</sub>	
At 0.59 pCt. NaCl	—	10 pCt.	—	} Haemoglobin had been set free.
" 0.57 " "	—	25 "	—	
" 0.55 " "	11 pCt	35 "	10 pCt.	
" 0.53 " "	33 "	60 "	28 "	
" 0.51 " "	44 "	78 "	40 "	
" 0.49 " "	66 "	90 "	60 "	
" 0.47 " "	74 "	100 "	68 "	
" 0.45 " "	83 "	—	78 "	
" 0.43 " "	92 "	—	90 "	
" 0.41 " "	100 "	—	—	

1) HAMBURGER and HEKMA Biochem. Zeitschrift Bd. III and Bd. VII.

*Conversely the capacity of resistance does not change if the Ca is prevented from leaving the blood-corpuscles though all the other metal-ions should disappear.*

8. *Also washed new erythrocytes have a greater capacity of resistance than washed old erythrocytes.*

At any rate the objection to the results of the examination of anaemic blood is removed: the fact that anaemic blood contains more serum than normal blood can have no effect upon the capacity

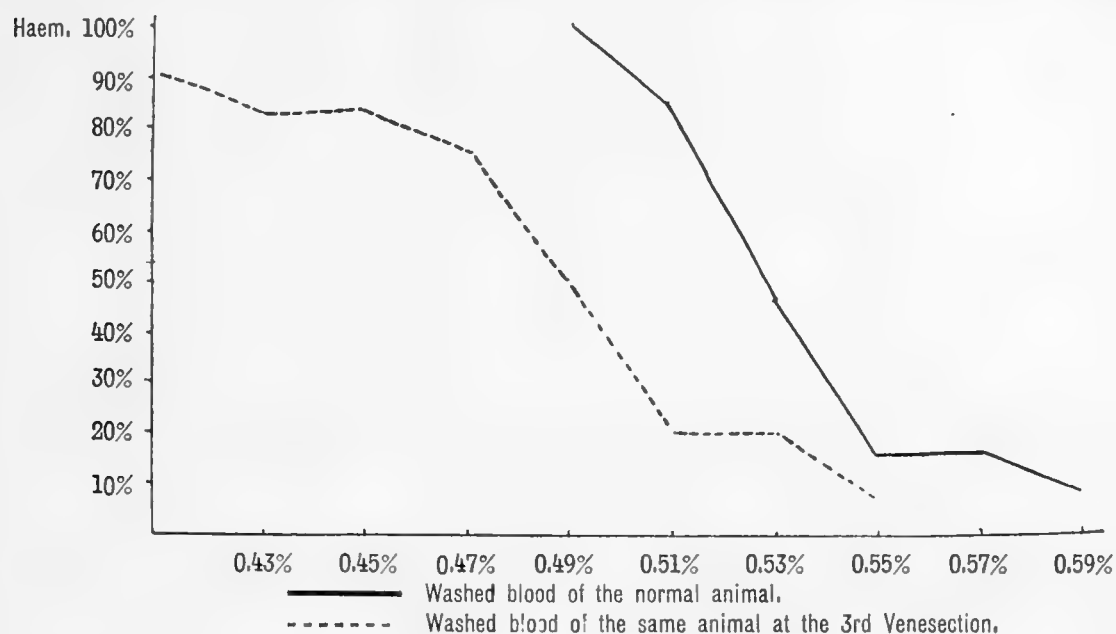


Fig. 6. Graphical representation of Table F.

TABLE F. Denoting the course of haemolysis in the normal and the anaemic animal after the blood-corpuscles have been washed with 0.9 pCt. NaCl.

	Normal blood (washed)	Anaemic blood (washed)
At 0.59 pCt. NaCl.	8½ pCt.	—
„ 0.57 „ „	16 „	—
„ 0.55 „ „	16 „	7½ pCt.
„ 0.53 „ „	46 „	20 „
„ 0.51 „ „	83 „	20 „
„ 0.49 „ „	100 „	50 „
„ 0.47 „ „	—	75 „
„ 0.45 „ „	—	82 „
„ 0.43 „ „	—	82 „
„ 0.41 „ „	—	90 „

} Haemoglobin had been set free.

of resistance as the serum contains *no* substances which impede haemolysis.

Moreover it may be observed that *also the washed blood-corpuscles of an anaemic animal possess a greater capacity of resistance than the washed blood-corpuscles of the same animal in a normal condition.* See Table F and Fig. 6.

### *Summary.*

The colorimetrical determination of the haemolysis, (ARRHENIUS) caused by diluted NaCl-solutions, suggests a means to compare the qualities of blood-corpuscles, differing as regards their capacity of resistance.

With the aid of this experimental method the following results were obtained.

1. New erythrocytes resist diluted NaCl-solutions better than old ones.
2. It must be assumed that new red blood-corpuscles are built up out of the old ones.
3. After venesections the regeneration greatly surpasses the loss. (Rule of WEIGERT).
4. Washing the blood-corpuscles with a NaCl-solution of 0,9 % renders them less capable of resisting diluted NaCl-solutions.
5. The conclusion drawn from this by several workers that this phenomenon is caused by the removal of unknown substances, found in the serum, which substances impede haemolysis, is incorrect. Experiments have shown that if a 4 % glucose-solution is used instead of a NaCl-solution 0,9 %, this decrease in capacity of resistance does not manifest itself.
6. The phenomenon, mentioned sub 4, should rather be viewed in the light of an osmotic disturbance, the principal factor of which is the loss of Ca, suffered by the blood-corpuscles. Indeed the capacity of resistance is not modified if 0,1 % CaCl<sub>2</sub> is added to the NaCl-solution.
7. New erythrocytes, washed with NaCl-solution 0,9 %, have a greater capacity of resistance than old ones which have been treated in the same way.

May 1912.

*Groningen, Physiological Laboratory.*

**Physics.** — “*Isotherms of diatomic gases and of their binary mixtures. X. Control measurements with the volumenometer of the compressibility of hydrogen at 20° C.* By W. J. DE HAAS. Communication N°. 127*a* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of April 26, 1912).

X. *The compressibility of hydrogen at 20° C.*

§ 1. *Introduction.* In Communication IX. “Control measurements with the volumenometer”, (Comm. N°. 121*a*, Proc. May 1911) a discussion based upon experimental data was given of the degree of accuracy attainable in determinations with the volumenometer. A determination of the compressibility of hydrogen at ordinary temperature has now given an additional desirable test of the accuracy with which the various experimental conditions in their mutual relationships have been fulfilled.

The investigation is based upon the Leiden measurements of the compressibility of hydrogen at pressures up to 60 atm. The accurate piezometers (Comm. N°. 50) and the sectional open manometer (Comm. N°. 44) specially designed by KAMERLINGH ONNES for that investigation rendered a very high accuracy attainable in those measurements. Considering this degree of accuracy, we may therefore take SCHALKWIJK’s measurements with those apparatus at 20° C. to be quite accurate, and ascribe the small difference between his formula and that deduced from AMAGAT’s results to a lower degree of accuracy in one or other of AMAGAT’s measurements (perhaps in his determination of the normal volume, which can be done more accurately by KAMERLINGH ONNES’s method). This conclusion is also supported by the fact that SCHALKWIJK’s formula is confirmed by the results obtained by KAMERLINGH ONNES and HYNDMAN (Comm. N°. 78).

We may therefore write at 20° C.

$$pv_A = 1.07258 + 0,000667 d_A + 0,00000099 d_A^2$$

in which  $p$  is the pressure,  $v_A$  the volume in terms of the normal volume and  $d_A$  is the reciprocal of  $v_A$ . On account of the small densities which occur in measurements made with the volumenometer (in which  $d_A$  is at the most 1.1) the  $d_A^2$  term may be neglected. The compressibility at 20° C. is then given by

$$\text{in which } \left. \begin{aligned} pv_A &= A_A + B_A d_A \\ A_A &= 1.07258 \\ B_A &= 0.000667 \end{aligned} \right\} \dots \dots \dots \text{(I)}$$

Again, on account of the small densities at which the volumenometer is used, the second of the terms on the right of the sign of equality plays but a small part in the result; it varies from  $7.10^{-4}$  of  $pv_A$  at density 1.1 to  $1.10^{-4}$  of  $pv_A$  at density 0.15. The question to be investigated in the proposed test was if compressibility determinations with the volumenometer could give values of  $pv_A$  to within  $2.10^{-4}$ .

As appears from the table at the end of § 3 giving  $pv_A$  as obtained from experiment and  $d_A$  as calculated, the accuracy attained in the compressibility determinations is as a rule somewhat greater than that which we desired. (Comm. No. 121, § 1). To show more clearly the nature of the remaining deviations, values of  $B_A$  determined by formula (I) have also been calculated from the volumenometer results by themselves; in doing this, of course, a sufficiently good approximation can be obtained only at the highest densities.

§ 2. *Summary of the experimental methods.* To get as good an idea as possible of the reliability of the volumenometer determinations of compressibility at temperatures between  $-252^\circ\text{C.}$  and  $-259^\circ\text{C.}$  the compressibility was first measured at ordinary temperature within the same pressure limits as would be chosen or were to be expected at the lower temperatures. Measurements were made with two distinct quantities of distilled hydrogen. For the first series a pressure of half an atmosphere was chosen as the starting point, and it was desired to ascend to a pressure of 1.1 atm. while in the second series the limits chosen were 0.16 atm. to 0.5 atm. The apparatus was filled in the usual way (cf. Comm. No. 94*f*) after repeated evacuations and washings with hydrogen.

For the determination at higher pressures measurements were made in the neck  $m_8$  (see Plate I, Comm. No. 117) and pressures were obtained from the manometer  $\Theta_B - \Theta_5$  and the barometer  $\theta_C - \theta_D$ . In this an artificial constant pressure practically equal to the barometric pressure was maintained in the manner usually adopted in the Leiden Laboratory by means of the ice pot  $R$ . To eliminate changes due to temperature fluctuations the four menisci to be observed were read twice in reverse order. Measurements were then made in the necks  $m_4$  and  $m_5$  (Pl. I loc. cit.). To do this the tap  $l_7$  was closed, and, keeping  $k_4$  closed, communication was established with a mercury pump through  $k_{41}$ ,  $k_{43}$ . After careful evacu-



ation the pressures of the volumes close to the necks  $m_4$  and  $m_5$  were measured, using the manometer as an indicator. For this two of the telescopes of the large Société Genevoise cathetometer were focussed upon the menisci in the volumenometer and manometer, and the heights were read each time from the standard metre  $S$ .

In an identical fashion measurements were made with a smaller quantity of gas in the necks  $m_3$ ,  $m_4$ , and  $m_5$ .

For further experimental conditions and precautions reference may be made to Comm. No. 121, § 4 and 5 and also to my dissertation, which is to be published shortly.

### § 3. Calculation and values of $pv_A$ .

The final value of the gas density for each of the two series of measurements, each with its own definite quantity of gas, was obtained by means of equation (I) from the observed final pressure after the application of the correction necessary for the small difference between 20° C. and the temperature at which the measurements were made. The pressure coefficient used was 0,0036627 (Comm. N°. 60). On account of the smallness of the temperature difference for which a correction has to be applied no correction is needed for the dependence of this pressure coefficient upon the pressure. The observed volumes  $v_A$  for each measurement follow from the  $v_A$ 's obtained from the final density and from the ratio of the volumes in each series measured at 20° C. to the final volume. Table I gives

No.	$t$	$p$	$d_A$ calc.	$pv_A$ obs.	O—C
1	20° C.	0.46780	0.43603	1.07278	— 0.00009
2	»	0.58113	0.54162	1.07295	+ 0.00001
3	»	1.12867	1.05161	1.07328	
1	20° C.	0.16310	0.15205	1.07247	— 0.00021
2	»	0.20258	0.18885	1.07248	— 0.00022
3	»	0.39313	0.36645	1.07282	

the values of  $pv_A$ , and those of  $d_A$  as calculated from  $p$  by means of equation (I).

From this it is evident that an accuracy of one in four thousand to one in five thousand is attained at the lower pressures, while in the series of measurements made at higher pressures the accuracy reached is greater than one in ten thousand.

§ 4. *Calculation of  $B_A$ .* From the former of the two series contained in Table I (pressures varying from 1.1 to 0.46)  $B_A$  can be calculated. Instead of  $B_{A20^\circ} = 0,00067$  it gives

$$B_{A20^\circ} = 0,00074 \text{ so that } O-C = 0,00007,$$

in which only the fourth decimal is significant. In the second series the percentage error expected in  $B_A$  is too great to allow of a calculation of  $B_A$  itself. Only under more favourable circumstances could one count upon an accuracy of one in ten thousand or more in the values of  $pv_A$ ; the error in  $pv_A$  becomes greater at smaller pressures; in  $B_A$  it is magnified four or five times and at small densities the utmost value of the whole term  $B_A d_A$  for that series is 0,00026. In the meantime it may be remarked that a comparison of the positive differences found here between observation and calculation (+0,0013) with the corresponding positive difference in the first series seems to indicate a possible systematic error which makes its presence specially felt at the lower pressures<sup>1)</sup>.

In order to be able to compare the results obtained with others which just had in view the determination of the compressibility at ordinary temperature we must reduce the results to a common basis.

Take first the measurements made by LEDUC<sup>2)</sup> at 16° C. and at pressures varying from 1 to 1.5 atmospheres. From the numbers which he obtains from his experiments after the incorporation of other data for the compressibility at 0° C. we find to correspond with his result

$$B_{A20^\circ} = 0,0007 \text{ and therefore } O-C = 0,0000.$$

The figure last given does not necessarily lead to the conclusion that the Leiden determinations with the volumenometer are the less accurate. The degree of accuracy of LEDUC's results is indicated by the fact that he goes only to the fourth decimal place (for CO<sub>2</sub>, CHAPPUIS<sup>1)</sup>) and LEDUC differ by 0,0002). And the pressures used by LEDUC in this determination, which is accurate to 1 in 10000 were very much more favourable (the smallest density was twice as great as that of the first series of Table I) than those which are expe-

<sup>1)</sup> Possibly a small constant error arising from a change in the correction for the capillary depression since the control measurement of Comm. N<sup>o</sup>. 121a.

<sup>2)</sup> A. LEDUC, Recherches sur les gaz. 1898.

rienced in experiments at liquid hydrogen temperatures and at which my measurements had to be made.

Determinations made by CHAPPUIS<sup>1)</sup> and by RAYLEIGH, in each case with apparatus designed to attain a higher degree of accuracy than that of the Leiden volumenometer, also afford a basis of comparison. CHAPPUIS measured compressibilities at 0° C. between 1.4 and 1.8 atmospheres. His results give  $B_{A0} = 0,00058$ , from which, using the figure given by KAMERLINGH ONNES and BRAAK<sup>2)</sup> for the difference between  $B_{A100^\circ}$  and  $B_{A0^\circ}$  we get

$$B_{A20^\circ} = 0,00064 \text{ and } O-C = -0,00003.$$

The values deduced from the two single observations distant by about half the pressure difference from each other, in which the errors are increased, differ by 0,0001.

Finally, Lord RAYLEIGH's<sup>3)</sup> measurements were made with an apparatus specially designed to give an accurate comparison between  $p v_A$  at half an atmosphere and its value at double that pressure. From them we get  $B_{A10.7} = 0,00054$  from which, using again the KAMERLINGH ONNES—BRAAK result just given, we obtain

$$B_{A20^\circ} = 0,00057 \text{ and } O-C = -0,00010.$$

So that comparison between the results now given with those yielded by these different researches shows a satisfactory agreement.

In the proposed determination of  $B_A$  at hydrogen temperatures circumstances will be much more favourable than at ordinary temperature, for  $B_A d_A$  will then be 15 to 20 times greater at the same pressure. We may regard the value obtained for  $B_A$  in this way at  $-252^\circ$  C. as accurate to within 2%, and to within 10% at  $-259^\circ$  C.

**Physics.** — “*Isotherms of diatomic gases and of their binary mixtures. XI. On determinations with the volumenometer of the compressibility of gases under small pressures and at low temperatures.*” By W. J. DE HAAS. Communication N<sup>o</sup>. 127<sup>b</sup> from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of May 25, 1912).

§ 1. *Criticism of the pressure equilibrium between the piezometer and the volumenometer.* In the investigation of the compressibility of hydrogen vapour with which a subsequent paper by Prof. KAMER-

<sup>1)</sup> P. CHAPPUIS, Nouvelles études sur le thermomètre à gaz.

<sup>2)</sup> Comm. no. 100<sup>b</sup>, These Proceedings Dec. '07.

<sup>3)</sup> Lord RAYLEIGH, Proc. Roy. Soc. 73 (1904). Ztsch. phys. Chem. 52 (1905).

LINGH ONNES and myself will deal, the volumenometer described in the previous Communication was used to measure the quantity of hydrogen contained under different pressures in a reservoir — the piezometer reservoir — which was immersed in liquid hydrogen and connected with the volumenometer by a capillary and tap. The pressure of the gas in the piezometer reservoir was then given for each measurement by the pressure of the gas in the volumenometer in pressure equilibrium with it. It was shown in Communications N<sup>o</sup>. 121<sup>a</sup> (Proc. May 1911) and N<sup>o</sup>. 127<sup>a</sup> (These Proc. p. 295) that the accuracy with which the pressure, volume and temperature of the quantity of gas contained in the volumenometer could be determined was sufficient to allow of the evaluation of the virial coefficients  $B$  at low temperatures for hydrogen vapour from determinations of the compressibility of that vapour. More particular attention must now be bestowed upon the question of pressure equilibrium between the volumenometer and the piezometer.

In the course of the above experiments it was repeatedly necessary to adjust the mercury in the volumenometer to one of the lower necks (for instance,  $m_1$ ,  $m_2$ , or  $m_4$ . Cf. Comm. N<sup>o</sup>. 117, Pl. I, Proc. Febr. 1911). The quantity of gas contained in the volumenometer was in those cases always less (though not many times) than that in the piezometer of 110 cc. capacity and at a temperature of  $-252^\circ$  to  $-258^\circ$  C., so that the gas in the piezometer was of a density from 12 to 20 times greater than that in the volumenometer. On each side of the capillary, therefore, which had to be long on account of the construction of the cryostat and narrow on account of the uncertainty of the volume correction to be applied for it, there are relatively large quantities of gas. On account of friction in the capillary, pressure equilibrium will be but slowly attained. A preliminary experiment had shown the desirability of a means to decide from the measurements themselves when exactly this pressure equilibrium had been attained. In order therefore to obtain the necessary data for this, the behaviour of the pressure in the volumenometer was systematically observed during the final experiments upon the compressibility of hydrogen vapour at low temperatures (June 23 and 24, July 8, 14, and 18, 1911) on each occasion on which the meniscus was adjusted to one of the necks  $m_1$ ,  $m_2$ ,  $m_3$ ,  $m_4$  — this of course only after satisfying the experimental conditions to be fulfilled for equilibrium (regulation of cryostat and of volumenometer thermostat, constancy of room temperature). At intervals, as a rule every 5 minutes, the difference between the levels of the mercury in the manometer and in the volumenometer was read and corrected, from

tables prepared beforehand, for changes occurring during the measurement in the quantities determining the corrections (such as change in the temperatures of the volumenometer, the piezometer, the dead-space, change in the capillary depression, etc.).

In this way the actual change in the difference between the pressure and the equilibrium pressure was known at all stages of the measurement. During the measurements a curve was drawn with this pressure difference as ordinate and time as abscissa, and the observation was regarded as at an end as soon as the plotted points began to fluctuate about a line drawn parallel to the abscissa axis. The accompanying diagram (unit ordinate representing 0.1 mm. mercury) is taken from the above investigation and refers to the adjustment of the pressure equilibrium on July 18, 1911, an occasion on which circumstances were particularly unfavourable. The observed pressure differences, increased by a certain fixed quantity, are represented by circles. At the end of § 3 we shall return to this diagram.

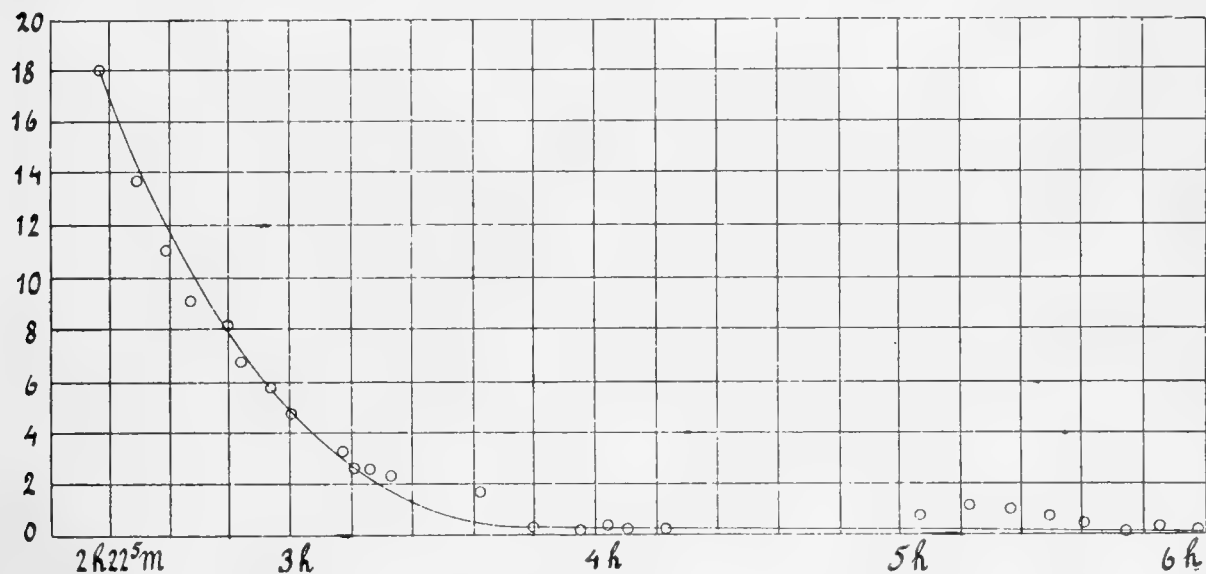


Fig. 1.

§ 2. *Calculation of the pressure change from the experimental data.*

The curve giving the change in the pressure difference between the two communicating vessels as a function of the time was now calculated from the dimensions of the apparatus and from data determining the temperature distribution along the glass capillary. As will be seen from the end of § 3, calculation is in complete agreement with observation, and is therefore suitable for checking the smallest pressure difference experimentally determined by the above method in the case discussed in § 3. The reduction of the theoretical calculation to formulae has the result that it not only covers this particular case, but it can also be applied to gauge the degree of pressure equilibrium in similar cases in which capillary connections occur in experiments at low temperatures.

The influence of gravity upon the gas is left out of account in the calculation, as is also the pressure difference which KNUDSEN's researches show must exist. If necessary both corrections may be applied to the observed pressure at which equilibrium is attained<sup>1)</sup>. The influence of slipping along the walls of the capillary is also left out of account, while the volume of the capillary has been regarded as negligible compared with that of the reservoir and of the volumometer. It is also assumed that the speed may be regarded as to remain the same over a short period of time, and that the speed is small (far below the critical); further that the temperature,  $T$ , and the pressure,  $p$ , may be regarded as uniform over any cross-section, so that if  $x$  is the length and  $y$  and  $z$  two axes at right angles to it and to each other,  $p$  is independent of  $y$  and  $z$ ; and, finally, that the speeds  $v$  and  $w$  in the directions of  $y$  and  $z$  may be taken to be zero. A flow is therefore assumed such that in a tube at constant temperature throughout and for a substance whose density is independent of the pressure POISEUILLE's law should hold, and such as may be regarded as subject to this law over any element of length,  $dx$ , of the capillary when the values of the pressure gradient, the density  $\rho$  and the viscosity  $\eta$  at that particular place are inserted. Working out the equations of motion subject to the given assumptions<sup>2)</sup> at once leads to the result

$$\frac{dm}{dt} = \frac{\pi}{8} R^4 \frac{\rho}{\eta} \frac{dp}{dx} \dots \dots \dots (1)$$

where  $m$  is the mass of the gas contained in the reservoir, and hence  $\frac{dm}{dt}$  the mass which flows per unit time across any section of the capillary.

We assume  $\eta$  to be independent of the pressure so that  $\eta = f(T)$ , and for  $f(T)$  we take SUTHERLAND's formula

$$\eta = \eta_0 \frac{1 + \frac{C}{273}}{1 + \frac{C}{T}} \sqrt{\frac{T}{273}}$$

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<sup>1)</sup> As a general rule, however, both corrections may be neglected. For the lowest pressure occurring in the course of the experiments for which this calculation was made the KNUDSEN correction just reached that limit at which the calculations by KAMERLINGH ONNES for the capillaries of his hydrogen and helium thermometers show it would begin to be appreciable.

<sup>2)</sup> Cf. O. E. MEYER, Pogg. Ann. 127. p. 253, 353.

in which  $C$  is a constant. As an approximation for vapours we may write  $p = a\varrho + b\varrho^2$  in which  $a$  and  $b$  are functions of  $T$ . These and all other quantities occurring in the present calculation were expressed in absolute measure (the C. G. S. system was chosen). If  $T$  be given as a function of  $x$ , equation (1) can at once be integrated.

As a further simplification for this integration we shall regard  $b$  as negligible on account of the smallness of  $b\varrho^2$  compared with  $a\varrho$ . If the pressure difference between the ends of the capillary is small, deviations from BOYLE'S law may, to the same extent, be allowed for. For further information on this point I may refer to my dissertation.

It may be further remarked that we may differentiate between three different portions of the capillary. The first part projects above the cryostat, and has throughout its whole length the same temperature, that of its surroundings (room temperature); for the pressure at the upper end of this portion we shall write  $p_4$  and for the pressure at the lower end  $p_3$ . In the second part of the capillary the temperature changes from the room temperature to that of the cryostat bath. The pressure at the upper end of this part is  $p_3$ , and for the pressure at the lower end we shall write  $p_2$ . The third portion of the capillary is wholly within the cryostat bath, and over its whole length has the temperature of the bath.  $p_2$  is the pressure at the upper end, and we shall write  $p_1$  for the pressure at the lower end.

With the object above indicated of not only calculating for the particular case discussed in § 3, but also of obtaining simple formulae applicable to analogous cases I have endeavoured to find a simple form for the function expressing the temperature of the middle portion in terms of the length; in order that four terms in this would suffice I have imagined a sudden change in the temperature at the junction of the second and third portions of the capillary, in other words I assume that at that point the temperature changes rapidly over a length which is large compared with the diameter of the capillary but is still small compared with its length.

The calculation is therefore made for a temperature distribution other than that which actually exists, but, as will be seen, the difference between the two cases does not affect the result.

The temperature distribution over that portion of the capillary in which the temperature is variable is thus represented by

$$x = q + l_x T + m_x T^2 + n_x T^3. \quad \dots \quad (2)$$

In the experiment further discussed in § 3 the temperature change

at the surface of the bath would be one of from  $T_2=26^\circ\text{K.}$  to  $T_1=15^\circ\text{K.}$

With  $a = a_1 T$ ,

$$k = \frac{1 + \frac{C}{273}}{\sqrt{273}} \quad \text{and} \quad A = \frac{8}{\pi R^4} \frac{dm}{dt}, \quad \dots \quad (3)$$

(1) now gives

$$\text{for the first portion} \quad A = \frac{1}{2\lambda_4 \eta_4 T_4} (p_4^2 - p_3^2), \quad \dots \quad (4)$$

$$\text{and for the third portion} \quad A = \frac{1}{2\lambda_1 \eta_1 T_1} (p_2^2 - p_1^2), \quad \dots \quad (5)$$

while the substitution of

$$T = C \operatorname{tg}^2 \alpha \quad \dots \quad (6)$$

gives

$$p_2^2 - p_3^2 = 4Aa_1 k \eta_0 C^{5/2} [(FT)_2 - (FT)_3] \quad \dots \quad (7)$$

in which

$$FT = \left[ \frac{nC^2}{3} \operatorname{tg}^3 \alpha + \frac{C(2m-3nC)}{7} \operatorname{tg}^7 \alpha + (l - 2mC + 3nC^2) \left( \frac{\operatorname{tg}^5 \alpha}{5} - \frac{\operatorname{tg}^3 \alpha}{3} + \frac{\operatorname{tg} \alpha}{1} - \alpha \right) \right], \quad \dots \quad (8)$$

so that  $p_2$  and  $p_3$  can be expressed in terms of  $p_1$  and  $p_4$ . From (4), (5), (7) it is seen that for a case such as that discussed in § 3 for which  $T_1 = 15^\circ\text{K.}$  and  $T_4 = 295^\circ\text{K.}$ ,  $p_1$  does not differ appreciably from  $p_2$ , so that one need not be very particular about the lower limit in the integral of (7) and (8), and the small jump in the temperature is of no influence within the limits of accuracy desired; this indeed is obvious if one considers that the gas flows about 20 times more slowly in the cold portion while the viscosity is also about as many times smaller.

With the temperature function now obtained for the interchange of pressure in a gas of known  $C$ ,  $\eta_0$  and  $a$ , through a capillary of radius  $R$ , and for a given temperature distribution, we obtain

$$\frac{dm_2}{dt} = \frac{\pi R^4}{8Ka_1} (p_1^2 - p_4^2) \quad \dots \quad (9)$$

in which  $m_2$  is the mass of gas in the volumenometer, and

$$K = L\eta_0 (FT_2 - FT_3) + M\eta_1 \lambda_1 T_1 + N\eta_4 \lambda_4 T_4$$

where the quantities  $L$ ,  $M$  and  $N$  follow at once from (4), (5) and (7). The first member of the expression for  $K$  refers to the portion of the capillary in which the fall of temperature occurs, and the second



and third members to those portions in which the temperature is uniform.

If we further write

$$p_1 = a_1 T_1 \frac{m - m_2}{v_1} \quad p_4 = a_1 T_4 \frac{m_2}{v_2} \quad . \quad . \quad . \quad (10)$$

in which  $v_1$  represents the volume at the lower temperature,  $v_2$  that at ordinary temperature, and  $m$  the total mass, and then integrate (9) we obtain, with the omission of an integration constant

$$\frac{v_1 v_2}{T_1 T_4 m} \log \frac{(m - m_2) + \frac{T_4 v_1}{T_1 v_2} m_2}{(m - m_2) - \frac{T_4 v_1}{T_1 v_2} m_2} = \frac{\pi R^4 a_1}{4 K} t \quad . \quad . \quad . \quad (11)^1$$

The case discussed in § 3 and graphed in fig. 1 gives an example of the curves given by this equation.

### § 3. *Application to a special case. Deductions.*

From measurements made during the experiment of 18<sup>th</sup> July 1911 temperatures were to be taken as

—258° C.	for 10 cm.	in the liquid bath
—228°	„	7 cm.
—115°	„	7 cm.
— 25'	„	14 cm.

Room temp. at + 22° „ 22 cm. projecting outside the cryostat.

For the calculation of (2) the temperature of each portion is regarded as the temperature at its centre.

We therefore get  $\lambda_1 = 10$ ,  $\lambda_4 = 11$ ,  $T_1 = 15$ ,  $T_4 = T_3 = 295$ ; and from  $x = 10$  to  $x = 49$  equation (2) holds with the values

$$q = 1.66 \quad l_x = 0.389 \quad m_x = -0.00278 \quad n_x = 0.00000682;$$

<sup>1)</sup> In the simple case in which  $p_1 + p_2$  may be regarded as constant, and  $T_1 = T_4$ ,  $m = v_1 d + v_2 d$  in which  $d$  is the common density in both vessels, substitution of (10) in (11) gives

$$\frac{v_1 v_2}{C_1(v_1 + v_2)} \log \frac{C_2}{p_1 - p_2} = C_3 t.$$

The subscript 4 is here replaced by 2.

This is the formula given by RAYLEIGH *Scientif. papers* Vol. IV 1892—1901 p. 53. This formula does not hold for instance for the evacuation of a vessel by a pump through a capillary, to which (11) is applicable as long as the pressure is not so small that the mean free path becomes comparable with the diameter of the capillary.

while, as was already remarked, the temperature jump assumed to take place at the surface of the liquid has no influence upon the result. We also find

$$m = 0,017, v_1 = 110, v_2 = 1035.$$

The line drawn in fig. 1 has been calculated from these data. The observed pressures, indicated by circles, agree well with the results of calculation.

Between half-past four and five more liquid gas was admitted into the cryostat. The readings during which the resulting pressure interchange was stopped by means of a valve are not marked in the figure. A slight temperature fluctuation occasioned by the refilling is clearly seen in the diagram. A small pressure increase at 5<sup>h</sup>5<sup>m</sup> dies down about six o'clock quite in accordance with the calculated curve. (See 3<sup>h</sup>27<sup>m</sup>. At this point the temperature also increased).

As can be seen, it took more than an hour for the last 1.8 m.m. pressure difference to die down to 0.02 m.m. (the whole pressure was 5 cm.).

The calculations show that the assumed distribution of temperature along the capillary is, in the main, correct. It gives a very welcome estimate of the time requisite for the last appreciable interchange of gas.

To establish pressure equilibrium as rapidly as possible in such experiments it is necessary that:

1. as little of the capillary as possible should project above the cryostat, and that the stem within the cryostat should be kept as cold as possible;
2. the upper part of the capillary should be wider than the lower, as is the case, for instance, in the helium thermometer of KAMERLINGH ONNES, or better still, the connecting capillary should be gradually narrowed. (In fig. 5 Comm. Suppl. N<sup>o</sup>. 21b<sup>1</sup>) compare the tube which, in the experiments by KAMERLINGH ONNES on the attainment of the lowest possible temperatures, had to carry off helium vaporised under a pressure of 0.2 mm. with the least possible reduction of pressure; the dimensions of this tube were calculated according to the principles of § 2).

*(To be continued).*

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<sup>1</sup>) Bericht über den II. Internationalen Kältekongres, Wien, October 1910, Bd. II.

**Physics.** — “*On the HALL effect and the change in the resistance in a magnetic field at low temperatures. I. Measurements on the HALL-effect and the change in the resistance of metals and alloys in a magnetic field at the boiling point of hydrogen and at lower temperatures*”. By H. KAMERLINGH ONNES and BENGT BECKMAN. Communication N<sup>o</sup>. 129<sup>a</sup> from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 29, 1912).

§ 1. *Introduction.* An investigation of the HALL effect and of the change of resistance produced by a magnetic field was carried out by VAN EVERDINGEN at Leiden some time ago down to liquid air temperatures<sup>1)</sup>, but the fundamental importance of these phenomena in the theory of electrical conduction has long made it desirable to extend this investigation to the much lower temperatures which have been freely available since the successful development of methods of obtaining accurate series of observations at liquid hydrogen temperatures. The problem, however, has been forced aside by other researches which could not be delayed, until the study of it and of allied problems for various metals at the lowest possible temperatures has been rendered essential to the further development of the theory of electrons by the discovery of the fact that the resistance of pure mercury disappears at liquid helium temperatures. We have therefore been occupied for some time with various aspects of the investigation of these problems at hydrogen temperatures, and, while we propose to continue this investigation systematically and, if possible, to make some measurements on the more important points at those temperatures which are obtainable with liquid helium, we give in the present paper some results which have already been obtained, and which may be considered to be themselves of some importance.

The investigation has been extended by one of us (B. BECKMAN) with the same experimental material to temperatures obtainable with liquid ethylene, liquid oxygen, and liquid nitrogen, and these results will be discussed in a later paper.

We wish to record our heartiest thanks to Mrs. A. BECKMAN for her assistance in the course of the measurements.

<sup>1)</sup> The results for bismuth (and antimony) given in the dissertations of LEBRET (Leiden 1895) and VAN EVERDINGEN (Leiden 1897) and in Communications Nos. 19, 26, 37, 40, 53, 58, 61 have been confirmed by BLAKE, *Ann. d. Physik.* **28**, 449, 1909 and LOWNDS, *Ann. d. Physik* **9**, 677, 1902. LOWNDS investigated rods cut in different directions from bismuth crystals, and extended his investigation for one direction down to liquid air temperatures. He found that with the crystalline axis perpendicular to the field the HALL coefficient is negative at higher temperatures, while as the temperature is lowered it vanishes and then becomes positive.

I. *Bismuth.*§ 2. *Change in the resistance of a wire of electrolytic bismuth.*

This part of the investigation was made with a wire of electrolytic bismuth provided by HARTMANN and BRAUN 0,3 mm. thick, and identically the same as that used by KAMERLINGH ONNES and CLAY in their determination of the change of resistance (Comm. N<sup>o</sup>. 99). The KOHLRAUSCH method of overlapping shunts was used. At ordinary temperature and at the boiling point of hydrogen the main current was 4 milliamps, but at  $-259^{\circ}$  C. it had to be reduced to 0.1 à 0.2 milliamps on account of the effect of heating upon the resistance. In the following Table  $w'$  represents the value of the resistance in ohms in a magnetic field of strength  $H$ ,  $w_T$  is the resistance with no field on, and  $w_0$  is the resistance at  $0^{\circ}$  C. with no field.

We may notice that we have not obtained the maximum in the isopedals observed by BLAKE. It will be seen from the forthcoming paper on the change of resistance with magnetic field at liquid air temperatures that BLAKE's bismuth wires which showed the maximum exhibited a smaller change in the resistance than ours and were therefore probably not so pure. It is possible that as the purity increases the maximum in the isopedals is displaced towards the lower temperatures.

$H$ Gauss	$T = 290^{\circ}$		$T = 20^{\circ},3$		$T = 15^{\circ}$	
	$w'$	$\frac{w'}{w_0}$	$w'$	$\frac{w'}{w_0}$	$w'$	$\frac{w}{w_0}$
0	2.570	1.057	0.588	0.242	0.526	0.216
2760	2.770	1.140	11.5	4.73		
3850	—	—	—	—	19.9	8.185
5540	3.110	1.280	32.8	13.50	34.9	14.35
7370	3.473	1.388	54.7	22.50	55.9	23.00
9200	3.635	1.495	76.7	31.55	80.8	33.25
11850	4.002	1.646	113.2	46.55	116.4	47.90
13600	4.248	1.746	141.5	58.20	143.1	58.85
15670	4.540	1.868	172	70.75	175.6	72.25
17080			196.5	80.85	199.3	82.00

The general character of the isotherms is also conserved at hydrogen temperatures; the field at which the resistance begins to increase practically proportionally to the field itself is about 12000 gauss just as at liquid air temperatures. The gradual transformation from the change at small fields to the practically linear change in strong fields takes place in the same way at each temperature.

§ 3. *The HALL-effect and the increase of resistance for plates of compressed electrolytic bismuth. Experimental method.*

The method adopted was that developed and applied by LEBRET and VAN EVERDINGEN in their dissertations (see Suppl. N<sup>o</sup>. 2); in it all disturbing influences are eliminated. A diagram is given in Plate 3 of the Supplement quoted, and for all matters concerning the arrangements for measuring we may refer to Chapter I of that paper. Circular plates were used to which were soldered with Wood's alloy the primary and HALL electrodes as well as two auxiliary electrodes (placed on the diameter in the direction of the main current). All were point electrodes <sup>1</sup>).

Choosing our notation to correspond with that of the Supplement quoted let us write  $e$  for the potential difference between the HALL electrodes,  $I$  for the main current and  $d$  for the thickness of the plate. The HALL constant  $R$  is given by

$$R = \frac{ed}{HI}.$$

Let us also write  $R_s$  for the resistance of the secondary circuit outside the plate,  $r$  for the resistance of the shunt of the compensating circuit,  $q$  for a constant determined by the differential galvanometer employed, and  $R_d$  for the resistance determined by

$$\frac{1}{R_d} = \frac{1}{2} \left( \frac{1}{R_A} + \frac{1}{R_B} \right)$$

in which  $R_A$  and  $R_B$  are magnitudes obtained from the resistances of the compensating circuit with reversal of the main current when the field commutator stands in each experiment in the positions  $A$  and  $B$  respectively; we then obtain

$$R = rdq \frac{R_s}{HR_d}.$$

The change in the resistance was also measured as well as the HALL effect.

At ordinary temperature the bismuth plates showed no asymmetry

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<sup>1</sup>) VAN EVERDINGEN has solved the problem theoretically for point electrodes with circular plates.

in the HALL-effect, but they showed it very clearly and sometimes very strongly at hydrogen temperatures, giving considerable differences between  $R_A$  and  $R_B$ . In the following tables twice the asymmetry is given by the side of the mean HALL-constant; for the method of evaluating the asymmetry we may again refer to Chapter I of Suppl. N<sup>o</sup>. 2. All quantities except  $w$  are expressed in C.G.S.

The current in the main circuit was  $I = 0.15$  amp. A WIEDEMANN galvanometer was used. The bath of liquid gas in the magnetic field was obtained in a silvered vacuum vessel by the method of Comm. N<sup>o</sup>. 114.

§ 4. *Results of the measurements.*

$Bi_{pI}$ ,  $Bi_{pII}$ ,  $Bi_{pIII}$ , represent three plates of 10 mm. diameter prepared from the same HARTMANN and BRAUN electrolytic bismuth.  $Bi_{pI}$  was compressed from a thin rod in a steel mould.  $Bi_{pII}$  and  $Bi_{pIII}$  were prepared by first grinding the bismuth to a fine powder in an agate mortar and then compressing in the same mould as  $Bi_{pI}$ . In the preparation of  $Bi_{pIII}$ , which was otherwise the same as that of  $Bi_{pI}$  and  $Bi_{pII}$ , the grinding operation took place in an atmosphere of carbon dioxide.

TABLE II								
The HALL constant, asymmetry and resistance change for $Bi_{pI}$ .								
$H$	$T = 289^\circ$				$T = 20^\circ,3$			
	$RH$	$2 \times \text{Asym.}$	$-R$	$\left[\frac{w'}{w}\right]_T$	$RH$	$2 \times \text{Asym.}$	$-R$	$\left[\frac{w'}{w}\right]_T$
2060	$13.9 \times 10^3$	$0.4 \times 10^3$	6.75	1.06	$91.4 \times 10^3$	$39.6 \times 10^3$	44.35	10.1
3450	20.9	0.2	6.06	1.12	166.5	48	48.25	21.7
5660	29.1	1.1	5.14	1.21	308	54	54.40	39.3
7160	33.2	0	4.64	1.29	385.5	114.5	53.90	52.0
9880	40.3	1.8	4.08	1.45	563	199	57.00	78.2
11090	42.6	2.3	3.84	1.50	640	243	57.70	89.5
0	$w_T = 0.00209 \ \Omega$				$w_T = 0.00044 \ \Omega$			
					$\frac{w_{20K}}{w_{289K}} = 0.22$			

With no field the ratio of the resistance of  $Bi_{pI}$  at hydrogen temperature to that at ordinary temperature is almost the same as the same ratio for the bismuth wire  $Bi_{dI}$ ; but in a magnetic field

TABLE III. HALL-constant, asymmetry and change of resistance for  $Bi_p II$ 

$H$	$T = 289^\circ$					$T = 20^\circ.3$					$T = 14^\circ.6$				
	$RH$	$2 \times \text{Asym.}$	$-R$	$\left[\frac{w'}{w}\right] T$		$RH$	$2 \times \text{Asym.}$	$-R$	$\left[\frac{w'}{w}\right] T$		$RH$	$2 \times \text{Asym.}$	$-R$	$\left[\frac{w'}{w}\right] T$	
	2060	$18.7 \times 10^3$	$0.2 \times 10^3$	9.08	1.023		$152.5 \times 10^3$	$24 \times 10^3$	74.1	1.71		$167.5 \times 10^3$	$3 \times 10^3$	81.3	1.788
3450	28.2	0.2	8.17	1.057	230	29	66.7	2.31	2.42	262	5.5	75.9	—	2.42	
5660	39.85	0.4	7.05	1.108	349.7	37.5	61.8	3.28	—	—	—	—	—	—	
7160	46.1	0.3	6.44	1.148	431.2	50	60.3	3.93	4.14	509	14	71.1	—	4.14	
8520	52.15	0.8	6.12	1.186	503	76	59.0	4.58	—	—	—	—	—	—	
9880	55.9	0.2	5.66	1.222	583	79	59.0	5.21	5.47	687	20	69.5	—	5.47	
11090	59.95	0.8	5.41	1.26	647.5	91	58.4	5.76	6.07	755	11	68.1	—	6.07	
12090	62.8	1.4	5.19	1.287	700	100	57.9	6.25	6.51	818	20	67.7	—	6.51	
0	$w_{289} = 0.00389 \Omega$					$w_{20} = 0.00487 \Omega$									

the ratio of the resistance at hydrogen temperature to the zero resistance is less for the disc than for the wire  $Bi_{dI}$ , so

$$\text{for } H = 11090 \text{ at } T = 20.3 \quad \begin{array}{cc} \text{disc} & \text{wire} \\ \frac{w'}{w_0} = 19.7 & \frac{w'}{w_0} = 42. \end{array}$$

In the case of  $Bi_{pII}$  both the negative temperature coefficient and the smallness of the change of resistance with magnetic field indicate the presence of impurities.

TABLE IV.				
The HALL constant, asymmetry and resistance change for $Bi_{pIII}$ .				
$H$	$T = 20^\circ$ .			
	$RH$	$-R$	Asym.	$\left[\frac{w'}{w}\right]_T$
2850	$247 \times 10^3$	86.6	$137 \times 10^3$	2.16
4700	426	90.7	210	2.91
6675	624	93.5	280	3.67
8275	814	98.5	346	4.44
10160	1007	99.2	400	5.12
11100	1105	99.4	425	5.49
12220	1216	99.5	460	5.87

With the disc  $Bi_{pIII}$  measurements were made only at hydrogen temperatures, but we give the results here as, just as with  $Bi_{pI}$ ,  $R$  increases with  $H$ , and approaches a limiting value, approximately **100**; this is the highest HALL coefficient yet obtained for bismuth.

All the coefficients we have obtained for bismuth plates are *negative*. Circumstances which give rise to positive <sup>1)</sup> coefficients occur only in certain positions of the crystalline axis and therefore, since all positions of the axis occur at random, they are obscured by those which give rise to negative coefficients.

## II. Other Metals.

§ 5. *Experimental method.* This was just the same as for bismuth. A THOMSON differential galvanometer was used for observing the HALL effect. Now the contacts were not soldered with WOOD'S alloy, but with tin.

<sup>1)</sup> Here total coefficients are considered, cf. Comm. N<sup>o</sup>. 129c. [Note added in the translation].



§ 6. *HALL effect for Gold.* The plate  $Au_{pI}$  was prepared from a dutch 10 fl.-coin; this was dissolved in aqua regia, precipitated by  $SO_2$ , melted in a porcelain crucible and rolled between steel rollers. During the last operation and afterwards it was treated with various acids. From the decrease with temperature of the resistance with no magnetic field (see Table V) it is seen that this plate was made of purer gold than that which composed the wire  $Au_0$  of Comm. N°. 99, which gave  $w_{T=20}/w_{T=273} = 0,045$  and was known to contain 0,03 % impurity.

$d$  was 0,101 mm.,  $I$  approximately 1.2 amp., and  $R_s = 0,6$  to 0,7 ohms.

We found :

$H$	$T = 290^\circ$		$T = 20.3^\circ$		$T = 14^\circ.5$	
	$RH$	$R \cdot 10^4$	$RH$	$R \cdot 10^4$	$RH$	$R \cdot 10^4$
7730	5.62	7.27	7.57	9.79	7.56	9.78
9500	6.75	7.11	9.32	9.81	9.22	9.71
11080	8.11	7.32	10.91	9.84	11.03	9.96
12220	8.85	7.25	11.98	9.81	12.00	9.82
$w_{T=290} = 202 \cdot 10^{-6} \Omega$			$w_{T=20,3} = 6,7 \cdot 10^{-6} \Omega$			

§ 7. *HALL effect for Silver.* The plate  $Ag_{pI}$  was prepared from

$H$	$T = 290^\circ \text{K.}$		$T = 20^\circ.3 \text{K.}$		$T = 14^\circ.5 \text{K.}$	
	$RH$	$R \cdot 10^4$	$RH$	$R \cdot 10^4$	$RH$	$R \cdot 10^4$
4940	3.97	8.04	—	—	—	—
726)	5.81	8.01	7.39	10.18	7.22	9.95
9065	7.23	7.98	9.22	10.17	8.98	9.91
10270	8.16	7.95	10.34	10.07	10.12	9.85
$w$	$173 \cdot 10^{-6} \Omega$		$1.47 \times 10^{-5} \Omega$		$0.925 \times 10^{-6} \Omega$	
$w/w_0$	1.065		0.00905		0.0057	

silver for which we are indebted to the Master of the Royal Mint, Dr. C. HOITSEMA. The silver was found to be practically the same as that of the wire  $Ag_I$  of Comm. N<sup>o</sup>. 99, which had 0,18 % impurity, and for which  $w_{T=20} w_{T=273} = 0,0089$  (cf.  $w_T$  in Table). The thickness of the plate,  $d = 0,096$  mm.

§ 8. *HALL effect for electrolytic Copper.* The electrolytic copper was supplied by FELTEN and GUILLAUME;  $d$  was in this case 0,057 mm. We found :

$H$	$T = 290^\circ \text{K.}$		$T = 20^\circ \text{K.}$		$T = 14^\circ.5 \text{K.}$	
	$RH$	$R \cdot 10^4$	$RH$	$R \cdot 10^4$	$RH$	$R \cdot 10^4$
7260	3.59	4.95	4.79	6.60	4.79	6.60
9065	4.42	4.87	6.03	6.65	5.94	6.55
10270	5.08	4.95	6.78	6.60	6.71	6.54
$w$	$312 \cdot 10^{-6} \Omega$		$2.94 \cdot 10^{-6} \Omega$		$2.83 \cdot 10^{-6} \Omega$	
$w/w_0$	1.065		0.0103		0.00907	

§ 9. *HALL effect for Palladium.* The plate  $Pd_{pI}$  was supplied by HERAEUS;  $d = 0,100$  mm. We found :

$H$	$T = 290$		$T = 20^\circ.3$		$T = 14^\circ.5$	
	$RH$	$R$	$RH$	$R$	$RH$	$R$
8250	5.61	$6.80 \times 10^{-4}$	11.42	$13.83 \times 10^{-4}$	11.54	$13.98 \times 10^{-4}$
9065	6.04	6.66	—	—	—	—
9360	—	—	12.71	13.58	12.96	13.84
9760	6.64	6.80	—	—	—	—
10270	—	—	14.0	13.63	14.09	13.74
$w$	$126.2 \times 10^{-5} \Omega$		$6.11 \times 10^{-5} \Omega$		$5.77 \times 10^{-5} \Omega$	
$w/w_0$	1.065		0.0515		0.0485	

The plate was annealed and was kept from contact with the liquid hydrogen in the bath by a coat of celluloid dissolved in amyl acetate. By immersing the same plate unprotected in the bath, so that it absorbed a large quantity of hydrogen it was found that the occlusion of hydrogen constantly diminished the HALL coefficient, as is evident from a comparison of the following data with those of Table VIII. It was observed that the change of resistance with temperature diminished at the same time. We found :

	at $T = 20^\circ \text{K.}$	$R = 12,0 \cdot 10^{-4}$	$w = 5,3 \cdot 10^{-5} \text{ Ohm.}$
then	„ $T = 290^\circ$	$R = 6,3 \cdot 10^{-4}$	$w = 107 \cdot 10^{-5}$
and again	„ $T = 14^\circ.5$	$R = 9,4 \cdot 10^{-4}$	
	„ $T = 20^\circ.3$	$R = 10,4 \cdot 10^{-4}$	$w = 6,9 \cdot 10^{-5}$
finally	„ $T = 290^\circ$		$w = 109 \cdot 10^{-5}$

§ 10. *Summary of results dealing with the change in the HALL coefficient for various metals.* In the two subsequent Tables we give figures for the change in the HALL coefficient when the temperature sinks to hydrogen temperatures and in the region of liquid hydrogen temperatures;  $R$  is the mean value taken from the previous tables at each definite temperature for each substance.

TABLE IX.  
The HALL coefficient  $R$  at hydrogen temperatures.

$T$	$Au_{pl}$	$Ag_{pl}$	$Cu_{pl}$	$Pd_{pl}$
$290^\circ$	$7.24 \times 10^{-4}$	$8.00 \times 10^{-4}$	$4.92 \times 10^{-4}$	$6.75 \times 10^{-4}$
$20^\circ.3$	9.81	10.14	6.62	13.68
14.5	9.82	9.91	6.56	13.85

TABLE X.  
Change of the HALL coefficient  $\frac{R_T}{R_{290^\circ K}}$   
on cooling to and in the region of liquid  
hydrogen temperatures.

$T$	$Au_{pl}$	$Ag_{pl}$	$Cu_{pl}$	$Pd_{pl}$
$290^\circ$	1	1	1	1
$20^\circ.3$	1.355	1.265	1.345	2.03
14.5	1.355	1.24	1.335	2.05

The change of the HALL coefficient on cooling to the temperature of liquid air  $\frac{R_{T=82}}{R_{T=293}}$  has been found by SMITH<sup>1)</sup> to be

1.03 for *Au*, 1.095 for *Ag*, and 1.205 for *Cu*.

It seems to be of great importance that the change in the HALL coefficient for *Ag* and *Au* takes place chiefly below  $-190^{\circ}$  C. and becomes practically constant again in the region of liquid hydrogen temperatures. This is also seen to be the case for palladium on comparison of the results of experiments by BENGT BECKMAN upon palladium at liquid air temperature, which are not in agreement with those given by SMITH, and which will be published in the forthcoming paper by BENGT BECKMAN. In connection with the different behaviour for copper, for which BECKMAN has already found an increase in liquid air although smaller than that given by SMITH, the question arises if this cannot be accounted for principally by the influence of impurity. Experiments which we have already undertaken upon alloys — in § 12 we give one set of results — will enable us to decide the point.

§ 11. *Change of resistance of  $Au_{pI}$ ,  $Pd_{pI}$ ,  $Cu_{pI}$ , in a magnetic field.*

From the measurements with these plates only approximate results can be obtained for this change on account of the smallness of the change in the already very small resistance. In the following table results which were obtained in fields of from 10000 to 11000 gauss are reduced to a standard field of 10 kilogauss.

TABLE XI				
Change of resistance in a magnetic field				
$w'_T / w_T$				
<i>H</i>	<i>T</i>	<i>Au</i>	<i>Cu</i>	<i>Pd</i>
10 Kilogauss	20°3 K	1.017	1.14	1.0015
10        "	14°5		1.10	

While at ordinary temperature the change caused in the resistance by the field is extremely small, at hydrogen temperatures it becomes quite appreciable.

<sup>1)</sup> A. W. SMITH, Phys. Review, 30, 1, 1910.

## III. Alloys.

§ 12. *Gold-Silver.* On account of the usually great influence of admixture upon the HALL effect and upon the magnetic change of resistance it was thought desirable to investigate various kinds of alloys. We are already in a position to communicate details of the behaviour of one *solid solution*, viz. an alloy formed by fusing 2% by volume of silver with gold. The exact analysis we shall publish later.  $d$  was here 0,073 mm.

$H$	$T = 290^\circ$		$T = 20^\circ.3$		$T = 14^\circ.5$	
	$RH$	$R$	$RH$	$R$	$RH$	$R$
8250	5.70	$6.91 \times 10^{-4}$	5.60	$6.79 \times 10^{-4}$	5.44	$6.60 \times 10^{-4}$
9065	6.31	6.96	—	—	—	—
9360	—	—	6.46	6.90	—	—
9760	6.75	6.91	—	—	6.44	6.60
10270	7.08	6.90	7.01	6.83	6.80	6.62
0	$w = 3.81 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 1.045$		$w = 1.083 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.298$		$w = 1.080 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.297$	

Here we have

$$\frac{R_{T=20.3}}{R_{T=290}} = 0.985.$$

$$\frac{R_{T=14.5}}{R_{T=290}} = 0.955.$$

The observations show that down to hydrogen temperatures and in that region itself the HALL coefficient decreases slightly; both changes however are so small that they do not exceed the limits of the probable error.

## POSTSCRIPT.

IV. *Bismuth crystals.*

§ 13. *HALL-effect in bismuth crystals.* We were not very successful with some of our measurements upon the rods cut in various directions from a crystal which had been formerly used by VAN EVERDINGEN in his researches, and we had therefore meant to postpone the communication of our results until we had obtained a complete series of determinations for various positions of the axis; just as we go to press, however, the important paper by J. BECQUEREL in the Comptes Rendus for 24<sup>th</sup> June 1912 reaches us, so that we now publish the result which we had already obtained for the case treated by LOWNDS; it is given in the following Table.

TABLE XIII.					
HALL-effect in a Bismuth crystal with the axis perpendicular to the field.					
$T = 290^{\circ}$			$T = 20^{\circ}.3$		
$H$	$RH$	$R$	$H$	$RH$	$R$
2010	$20.0 \times 10^3$	- 9.95	1850	$18.0 \times 10^3$	+ 9.72
3740	30.6	- 8.18	3700	26.0	+ 7.03
5870	38.6	- 6.58	5800	33.6	+ 5.79
8250	42.1	- 5.11	8700	43.7	+ 5.02
10270	44.3	- 4.31	11080	53.1	+ 4.79

At hydrogen temperatures  $R$  is positive and approximates to a constant value; at ordinary temperature it is  $RH$  corresponding to negative values of  $R$  which approaches a constant value. It is possible that small impurities exert considerable influence upon these changes, and it would therefore be risky to conclude from the fact that the value of  $R$  at hydrogen temperature which we have found is not greater than that found by LOWNDS for one direction in liquid air, that no change of any importance takes place between the latter temperature and that of liquid hydrogen. (The resistance measurements show that LOWNDS's bismuth plate was freer from impurity than ours).



T A B L E XIV.

Linear variation of the HALL effect  
for  $Bi_{pII}$  in strong fields  $T = 20^{\circ}.3$  K.

$H$	$RH$ Obs.	$RH$ Calc.
3450	$230 \times 10^3$	$229 \times 10^3$
5660	350	352
7160	431	434
8520	503	507
9880	583	582
11090	647.5	647
12090	700	702

$$a' = a'_0 e^{-\beta' T}. \quad (4)$$

within the temperature region  $90^{\circ}$  K.  $\geq T \geq 14^{\circ}$  K. A much more complicated formula would be required to embrace the observations at higher temperatures as well.

On going down to liquid hydrogen temperatures the constant  $b'$ , the maximum value of the second BECQUEREL component, which is negative at ordinary temperature becomes positive in the case of  $Bi_{pI}$  and  $Bi_{pIII}$ . BECKMAN'S investigations upon the same plates at the temperature of liquid air show that the reversal of the sign must take place below  $72^{\circ}$  K.

*b.* With regard to crystals we have already stated in § 13 that, when the crystalline axis is perpendicular to the field, the HALL effect is negative at ordinary temperature, and approaches a limiting value. To this we may now add that with another rod also with its axis perpendicular to the field we found, at ordinary temperature, a maximum at  $H = 9500$ , and then a decrease ( $10^{-3} RH$  fell from 37 to 35.4); this leads us to suspect that proceeding to stronger fields than those we employed would have brought to light the same behaviour in the case of the rod quoted in § 13. At hydrogen temperatures the sign of the HALL effect reverses and becomes positive, increasing linearly with the field for fields above 3 kilogauss<sup>1</sup>). From this it appears that in

<sup>1</sup>) J. BECQUEREL draws attention to the fact that at low temperatures  $RH$  becomes very large. The values we here give for hydrogen temperatures make this all the more striking. For  $Bi_{pII}$  we obtained  $RH = 500 \cdot 10^3$  for  $H = 8500$ . With this plate, indeed, at the temperature  $T = 90^{\circ}$  K. we get a higher value ( $RH = 214 \cdot 10^3$  for  $H = 8500$ ) than that given by BECQUEREL for his plates. From his data (loc. cit.) we calculate for the temperature of liquid air  $RH = 168 \cdot 10^3$  (or  $R = +19.8$ ) for  $H = 8500$ .





**Physics.** — “*Magnetic Researches. VI. On paramagnetism at low temperatures*”. By H. KAMERLINGH ONNES and E. OOSTERHUIS : Communication n<sup>o</sup>. 129<sup>b</sup> from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 29, 1912).

§ 1. *Introduction.* In the present experiments which form a continuation of those discussed by KAMERLINGH ONNES and PERRIER in Comm. Nos. 122<sup>a</sup> and 124<sup>a</sup> we have again measured the attraction exerted by a non-homogeneous field upon a long cylinder of the experimental substance. Unless where we state otherwise, the experimental substance was finely powdered and contained in a glass tube just as was done in the researches referred to. In the present experiments, however, we adopted a device which had only been tried a few times in the former series, and, in order to eliminate the effect of the glass, the tube was taken twice as long as the part of it which contained the powder, so that the two halves were the same except that one was evacuated and the other held the powder ; the evacuated part was separated from the other by a plug of cotton wool which was placed in our experiments at about the centre of the field of our WEISS electro-magnet. We now balanced the attraction by gravity, and instead of allowing the tube to be drawn down by the attraction of the field and to be raised to its zero position electromagnetically, the tube was now drawn up by the action of the field and was brought down again to its zero position by weights. The modified form of the apparatus allowed much greater forces to be measured without involving any considerable alteration ; we shall return to its description whenever a detailed account is given of the apparatus used in the former experiments.

§ 2. *Anhydrous Ferrous-sulphate.* Comm. No. 124a stated that it was intended to investigate this substance at temperatures available with liquid nitrogen, so as to fix more definitely the temperature at which  $\chi$  attains its maximum value, which lay according to the experiments then made between 143° K. and 20° K. While this particular investigation was our principal aim, at the same time we repeated the measurements previously obtained at other temperatures. The salt was dried by heating for some time in vacuo to 280° C. special care being taken with this operation. We obtained the following results: (see table I, p. 323).

If we compare these with the results given in Comm. No. 124a for ferrous-sulphate which was practically anhydrous we see that a small admixture of water diminishes the value of  $\chi$ , and that to a

TABLE I  
Anhydrous ferrous-sulphate I.

$T$	$\chi \cdot 10^6$	$\chi \cdot T \cdot 10^6$	Limits of $H$	Bath
290° .2 K	67.6	19617	14000 - 16000	Room atmosphere
169.6	107.2	18181	14000 - 17000	Liquid ethylene
77.3	200.4	15491	} 14000—17000	Liquid nitrogen
70.4	215.1	15143		
64.8	227.3	14729		
20.1	402	8080	} 10000—16000	Liquid hydrogen
17.8	379	6746		
14.4	335	4824		

very large extent at hydrogen temperatures. For while the increase in the value of  $\chi$  brought about by more efficient drying is only a few percent at ordinary temperature, it is as much as 50% at 20° K. That we must really look in this direction for an explanation of the

TABLE II  
Ferrous-sulphate III. not quite anhydrous

$T$	$\chi \cdot 10^6$	Limits of $H$	Bath
289° .5 K	62.1	8000—17000	Room atmosphere
169 .6	95.7	9000—17000	Liquid ethylene
77 .3	169.8	} 5000—15000	Liquid nitrogen
70 .4	182.0		
64 .8	189.8		
20 .1	231.4	} 4000—17000	Liquid hydrogen
17 .8	220.6		
14 .4	204.8		

differences between the numbers given in November 1911 and those now communicated is evident from an experiment in which the quantity of moisture present in the ferrous-sulphate was purposely increased slightly (the quantity of water present being probably a little greater than that of ferrous-sulphate II, by which we designate

the specimen used by KAMERLINGH ONNES and PERRIER). For this not quite anhydrous ferrous-sulphate III we found the data given in table II (p. 323).

§ 3. *Deviations from CURIE's law.* In previous Communications an attempt was made to establish a law other than CURIE's (which from Table I does not hold for anhydrous ferrous sulphate) to represent empirically the variation of  $\chi$  with temperature; for this was given the law  $\chi\sqrt{T} = \text{const.}$ , which did quite well indeed represent the various observations then under consideration. The analogy of phenomena exhibited by ferric sulphate, which lead one to believe that this substance exhibits ferromagnetism at low temperatures, suggested to us to express  $\chi^{-1}$  as a function of the temperature, and we found that the formula  $\chi(T + \Delta') = C'$ , which has also been used by WEISS and FOËX<sup>1) 2)</sup> was worth trying with positive values of  $\Delta'$  and  $C'$ . As long as we keep above  $-208^\circ\text{C}$ . this formula is quite satisfactory for the representation of the deviations from CURIE's law at low temperatures found by KAMERLINGH ONNES and PERRIER and by us up to the present; we shall give several instances of this in § 7. The variation of  $\chi$  as a function of the temperature can then be expressed for ferrous sulphates of different degrees of dryness by ascribing different values to  $\Delta'$ . Below the maximum  $\chi^{-1}$  remains still linear, at least to a first approximation, but the constant,  $C''$ , which replaces the CURIE constant in that region, is negative, as is also  $\Delta''$ , the constant which replaces  $\Delta'$ .

The results obtained for ferrous sulphates I, II, and III are shown

1) Starting with the idea of corresponding states for para- and ferro-magnetic substances, we were led to the formula  $\chi(T + \Delta') = C'$  by an attempt to determine the absolute temperature  $\Theta$  of the possible CURIE point with the help of experimental data in the suspected region of the "magnétisme sollicité". We found  $\Theta$  negative, which brought to our minds the notion of the inverse field by which VOIGT has tried to explain certain peculiarities of the ZEEMAN effect as shown by salts of the rare earths. It was only after we had represented the deviations from CURIE's law shown by paramagnetic substances at low temperatures by means of this molecular diamagnetic field that we noticed that WEISS and FOËX had in the same way represented the behaviour of  $\gamma$ -iron and the nickel alloys above the CURIE point. WEISS and FOËX show that there is no prima facie cause why the WEISS molecular field could not occur with the opposite sign. It speaks well for the reasonableness of the hypothesis that we should be led to it for entirely different substances and under circumstances in which the quantity  $\frac{H}{T}$ , fundamental in paramagnetism, is so much greater than in the experiments made by WEISS and FOËX.

2) After this communication was printed in dutch, we received the dissertation of A. PREUSS, Zürich 1912, in which there is found also a negative molecular field for the alloys of Fe with less than 16% Co. [Note added in the translation.]

graphically in Fig. 1.  $C'$  and  $C''$  are seen to be practically equal

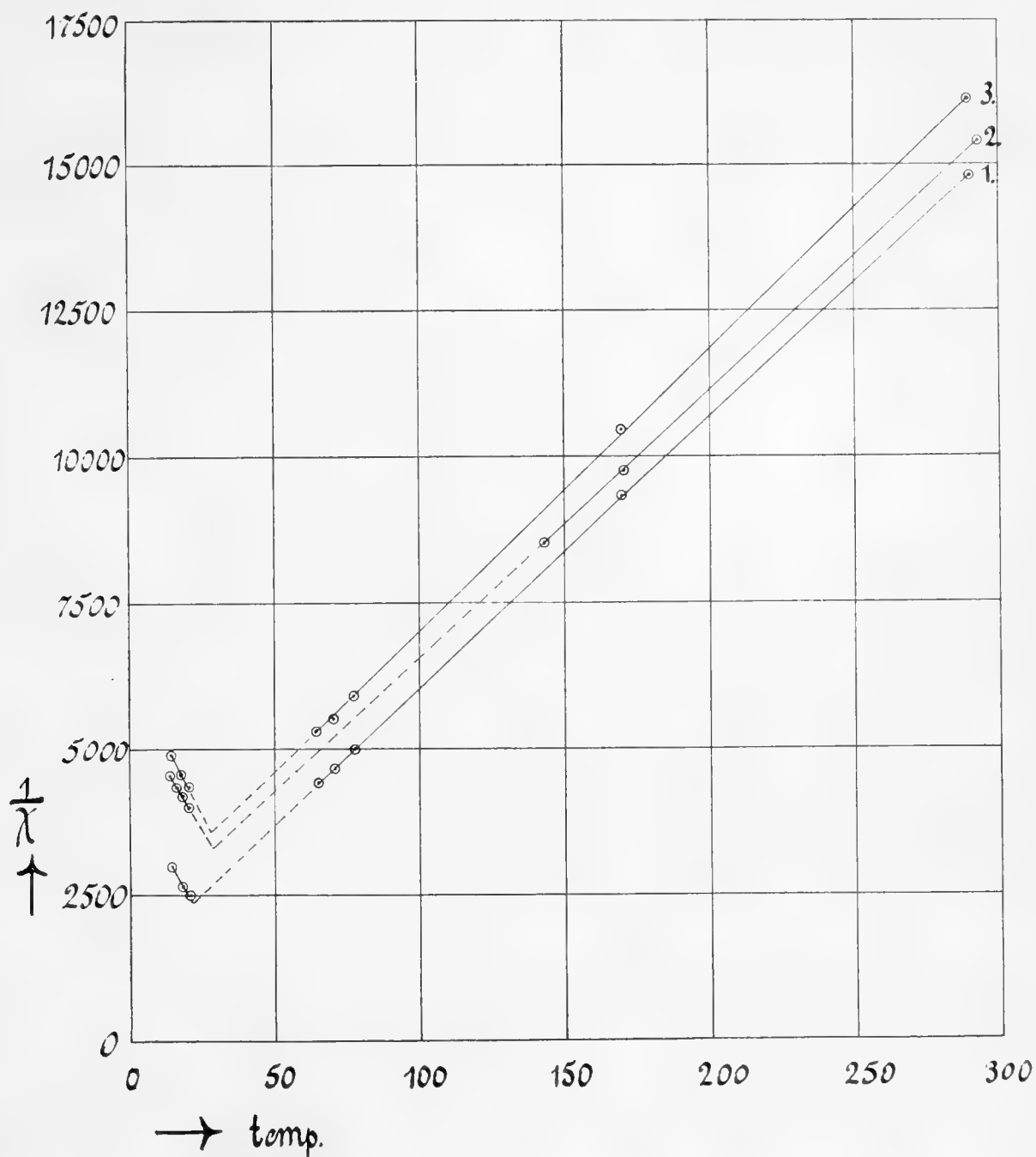


Fig. 1.

for the different degrees of dryness, while  $\Delta'$  ( $31^\circ$  for ferrous sulphate I) and  $\Delta''$  differ and increase in magnitude with the quantity of moisture present in the salt.<sup>1)</sup> The difference between the values of  $C'$  and  $C''$  for different degrees of dryness is so small that it practically coincides with the limits of accuracy of the observations. On the present representation the temperature at which  $\chi$  attains its

<sup>1)</sup> For crystallized ferrous sulphate the line, according to Table II, Comm. 122a of KAMERLINGH ONNES and PERRIER, is passing almost through the origin,  $\Delta'$  being  $2^\circ$  only. So, interposition of a small number of water molecules seems to increase  $\Delta'$ , of a great number to reduce it to a very small value. (Note added in the translation).

maximum value is given by the point of intersection of the two lines, which are determined by the constants  $C'$  and  $\Delta'$ , in the first disturbed paramagnetic state (we shall designate that state normal in which the CURIE law holds), and by the constants  $C''$  and  $\Delta''$  in the second disturbed paramagnetic state. The temperature of the maximum therefore alters with the quantity of moisture contained in the salt. It lies just above the boiling point of hydrogen, so that a new arrangement of the experiment is necessary before the correctness of this deduction can be tested and at the same time an investigation made as to whether the formula given holds good up to the maximum or not. That this is probably so is corroborated by the fact that on cooling ferrous sulphate I down to  $20^\circ$  K.  $\chi$  would increase continuously until it began to fluctuate about its mean final value, while on cooling ferrous sulphate III  $\chi$  clearly overstepped its maximum value before the temperature of the bath was reached, just as is to be expected from the diagram.

§ 4. *Anhydrous ferric sulphate down to  $-208^\circ$  C.* Anhydrous ferric sulphate was also investigated at the same time as the ferrous sulphate to ascertain any possible influence of the valency of the iron atom, and to see if  $\chi$  for ferric sulphate also reached a maximum value. Down to the temperatures available with liquid nitrogen and in that temperature region we found perfectly regular behaviour corresponding to what we have termed the first disturbed paramagnetic state. We found:

$T$	$\chi \cdot 10^6$	$\chi(T + \Delta') 10^6$ $= C' \cdot 10^6$	Limits of $H$	Bath
289° .8 K	53.3	17100	9000—15000	room atmosphere
169 .6	85.6	17170	7000—17000	liquid ethylene
77 .4	157.2	17040	} 14000—17000	liquid nitrogen
70 .5	167.3	16980		
64 .9	177.1	16980		

Valency, which plays such an important part in solutions, has here but a very slight influence down to and at nitrogen temperatures;

the difference between the molecular susceptibility of anhydrous ferric sulphate and that of ferrous sulphate I is only about 3%.

We may note that  $\Delta'$  is the same for both anhydrous ferrous and ferric sulphates.

For the behaviour of ferric sulphate at hydrogen temperatures we may refer to § 8.

§ 5. *Manganese chloride.* Manganese chloride was used which had been freed from water as far as possible; it was not possible to make it quite anhydrous. As can be seen from the following table it obeys CURIE'S law exactly at temperatures above  $-208^{\circ}\text{C}.$ ; values are also given for hydrogen temperatures for which the law no longer holds.

TABLE IV.				
Manganese chloride I, pulverised, not quite anhydrous.				
$T$	$\chi \cdot 10^6$	$\chi \cdot T \cdot 10^6$	Limits of $H$	Bath
290 <sup>o</sup> .8 K	106.5	30970	6000--17000 G	room atmosphere
169 .6	183.4	31100	5000--17000	liquid ethylene
77 .4	403	31190	5000--16000	} liquid nitrogen
70 .5	440	31020	7000--16000	
64 .9	480	31150	5000--16000	
20 <sup>o</sup> .1	1419	28520	5000--16000	} liquid hydrogen
17 .8	1589	28280	3000--10000	
14 .4	1881	27090	3000--16000	

§ 6. *Gadolinium sulphate.* The observations of KAMERLINGH ONNES

TABLE V.				
Crystallised gadolinium sulphate II.				
$T$	$\chi \cdot 10^5$	$\chi \cdot T \cdot 10^5$	Limits of $H$	Bath
293 <sup>o</sup> .1 K	68.9	20190	9000--17000	room atmosphere
20 .1	997	20049	5000--15000	liquid hydrogen

and PERRIER were supplemented by those included in table V (p. 327) which further confirm the validity of CURIE'S law and the absence of saturation phenomena.

This result, on account of the large number of magnetons present in gadolinium sulphate and of the resulting large value of the  $a$  of LANGEVIN at this low temperature is of importance to LANGEVIN'S theory, according to which saturation phenomena are here still outside the limits of experimental accuracy.

§ 7. *Summary of the deviations from CURIE'S law.* We here append the representation of the experiments of KAMERLINGH ONNES and PERRIER on dysprosium oxide (Comm. N<sup>o</sup>. 122<sup>a</sup>) by the formula  $\chi(T + \Delta') = C'$ .

TABLE VI.  
Dysprosium oxide  
represented by the formula  
 $\chi(T + \Delta') = C'$ ;  $\Delta' = 16$

$T$	$\chi \cdot 10^6$	$\chi(T + \Delta') \cdot 10^6$
288° .5 K	229.2	69790
170	374.6	69670
[132 .79	445.7	66320]
20 .25	1915	69420
17 .94	2032	68970
15 .95	2173	69430
13 .93	2334	69860

With the exception of the measurement made with liquid ethylene boiling under reduced pressure, which is rendered doubtful by the otherwise good agreement between observation and formula, the differences do not exceed the limits of experimental error.

If we collect the various data hitherto given in this paper the following different cases are seen to occur.

Gadolinium sulphate follows CURIE'S law over the whole region of low temperatures down to the lowest hydrogen temperature, 14° K, throughout the whole of this region we may call it a *normal* paramagnetic substance.

Over the whole region of low temperatures and down to the lowest hydrogen temperature dysprosium oxide obeys the law  $\chi(T + \Delta') = C'$



with  $\Delta'$  and  $C'$  positive. Over the whole of this region it shows therefore a disturbance of the first kind, which is to be ascribed to the occurrence of a WEISS molecular field of opposite sign.

Down to  $-208^\circ$  C., and perhaps lower, manganese chloride is normal. At hydrogen temperatures it deviates in a manner which may to a first approximation be represented by  $\chi(T + \Delta') = C$ , or, in other words, the disturbance throughout this region is of the first kind. Crystallised ferrous sulphate behaves in exactly the same way. (Comm. N<sup>o</sup>. 122<sup>a</sup>).

Both anhydrous ferrous sulphate I and ferrous sulphate not quite anhydrous (see § 3) show a disturbance of the first kind down to  $-208^\circ$  C. and probably to about  $-250^\circ$  C.; at hydrogen temperatures they show a disturbance of the second kind (both  $\Delta''$  and  $C''$  negative).

At low temperatures down to  $-208^\circ$  C. anhydrous ferric sulphate exhibits the same disturbance of the first kind as anhydrous ferrous sulphate. At hydrogen temperatures it exhibits the deviations which are discussed in the following section.

§ 8. *Ferric sulphate at hydrogen temperatures.* For the first time in the course of our observations we here found a dependence of the susceptibility upon the magnetic field which leads one to presume the existence at these temperatures of ferromagnetism in a substance which at ordinary temperatures is paramagnetic. We must in the meantime confine ourselves to this general remark. Accurate data giving magnetisation as a function of the field at different temperatures cannot be immediately deduced from the attractive force exerted upon a long cylinder in a non-homogeneous field, as long as  $\chi$  remains an unknown function of  $H$ . The investigation has therefore in the first place been continued with a cylinder of short length (a disc) of ferric sulphate placed in a certain part of the field at which both  $H$  and  $\frac{\partial H}{\partial x}$  are known.

We must refer to a subsequent paper for the results obtained and for the deductions which may be drawn from them.

**Physics.** — “*A theory of polar armatures.*” By H. DU BOIS. (Communication from the Bosscha-Laboratory).

A well-known partial theory for truncated cones was given by STEFAN and applied to the isthmus-method by Sir ALFRED EWING. As a first approximation the magnetisation of the poles is everywhere

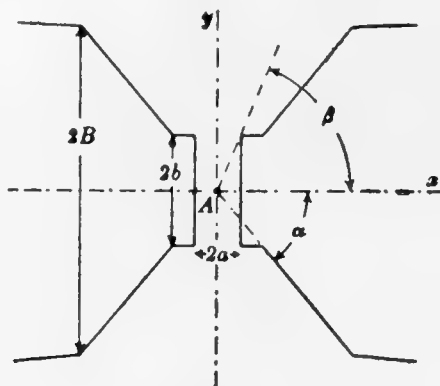


Fig. 1.

assumed parallel to the  $x$ -axis (Fig. 1) and thus polar elements have to be dealt with on the terminal surfaces only.

Now the magnetic field due to coils of various shapes has been thoroughly investigated in every detail by various authors, whereas that produced by ferromagnetic pole-pieces is only known for particular points in a few special cases. I believe it is now useful to develop a more general and complete theory for arbitrary points in the field, regard being also paid to protruding frontal surfaces, such as I have been using since 1889 (see fig. 1).

Considering the increasing introduction of prismatic pole-pieces, e. g. for string-galvanometers and other applications, I have also calculated equations for these, generally exhibiting a formal analogy with the conic formulae. Instead of a meridian section, Fig. 1 in this case represents a normal section, the generatrices being directed normally to the plane of figure and parallel to the  $z$ -axis.

For the determination of attraction or repulsion the first derivatives of the field with respect to the coordinates have to be considered; e. g. for gradient-methods in measuring weak para- or diamagnetic susceptibilities and also for extraction-magnets, such as those used in ophthalmologic surgery and in ore-separators.

Besides the intensity of the field its topography, especially its more or less uniform distribution appears more and more important in quantitative work and ought to be investigated. Here the second derivatives of the field also come in.

The following equations may occasionally serve as well for certain

electrostatic problems showing the same geometrical configuration, on account of the well-known general analogies. The details and proofs are to be given elsewhere.

*Round armatures.* Considering in the first place surfaces of revolution, more especially cones, the coincident vertices of which both lie in  $A$ , the field in this point is known to be

$$\mathfrak{H}^0 = \mathfrak{H}_1 + \mathfrak{H}_2 = 4\pi \mathfrak{J} \sin \text{vers } \beta + 4\pi \mathfrak{J} \sin^2 a \cos a \log \frac{B}{b} . . (I)$$

The notation sufficiently appears from Fig. 1. Both terms are generally of the same order practically; the first corresponds to the truncated frontal planes, the second to the conic surfaces; the latter shows a maximum for  $a = \tan^{-1} \sqrt{2} = 54^\circ 44'$ .

In order to judge of the field's uniformity we now consider the second derivatives, which are related to one another by LAPLACE'S equation and the symmetry of the case. The  $x$ -component,  $\mathfrak{H}_x$ , of the field is everywhere meant, though the index  $x$  is mostly omitted for simplification. For the centre  $A$ , where the first derivatives evidently vanish, the following values are found

$$\frac{\partial^2 \mathfrak{H}_1}{\partial x^2} = -2 \frac{\partial^2 \mathfrak{H}_1}{\partial y^2} = -2 \frac{\partial^2 \mathfrak{H}_1}{\partial z^2} = 4\pi \mathfrak{J} \frac{3 \sin^2 \beta \cos^3 \beta}{a^2} = 4\pi \mathfrak{J} \frac{3 \sin^4 \beta \cos \beta}{b^2} (1)$$

Now the term  $\mathfrak{H}_1$  always shows a minimum in the centre  $A$ , when passing along the longitudinal  $x$ -axis, corresponding to a maximum along the equatorial transverse axes, because the numerator  $\sin^2 \beta \cos^3 \beta$  remains positive for  $0 < \beta < \pi/2$ ; in particular this is a maximum, and accordingly the non-uniformity is greatest, for  $\beta = \tan^{-1} \sqrt{2/3} = 39^\circ 14'$ .

The term  $\mathfrak{H}_2$  behaves exactly in the opposite way, its second derivative vanishing for that same angle. This well-known result also follows from the general formula, which I now find, viz:

$$\frac{\partial^2 \mathfrak{H}_2}{\partial x^2} = -2 \frac{\partial^2 \mathfrak{H}_2}{\partial y^2} = -2 \frac{\partial^2 \mathfrak{H}_2}{\partial z^2} = 4\pi \mathfrak{J} \cdot \frac{3}{2} \sin^4 a \cos a (5 \cos^2 a - 3) \left( \frac{1}{b^2} - \frac{1}{B^2} \right) (2)$$

As  $B > b$  this expression evidently is  $\pm$  for  $a \lesseqgtr \cos^{-1} \sqrt{3/5} = 39^\circ 14'$ ; accordingly  $\mathfrak{H}_2$  shows a longitudinal minimum and transverse maximum for smaller semi-angles, whereas for larger ones the reverse holds, so as to make the field weaker on the axis than in its lateral surroundings. Finally for the total field

$$\frac{\partial^2 (\mathfrak{H}_1 + \mathfrak{H}_2)}{\partial x^2} = 4\pi \mathfrak{J} \frac{3}{2b^2} \left[ 2 \sin^4 \beta \cos \beta + \sin^4 a \cos a (5 \cos^2 a - 3) \left( 1 - \frac{b^2}{B^2} \right) \right] (3)$$

Equalizing the contents of the square brackets to zero gives a relation between  $\alpha$  and  $\beta$ . In most practical cases  $b^2/B^2$  may be neglected and we find

$$\begin{array}{l} \text{e. g. for } \alpha = 39^\circ 14' \quad \left| \quad 54^\circ 44' \quad \left| \quad 57^\circ \quad \left| \quad 60^\circ \quad \left| \quad 63^\circ 26' \right. \right. \\ \text{the value: } \beta = 90^\circ \quad \left| \quad 79^\circ 26' \quad \left| \quad 76^\circ 52' \quad \left| \quad 72^\circ 49' \quad \left| \quad 63^\circ 26' \right. \right. \end{array}$$

as corresponding sets. For the most favourable semi-angle  $\alpha = 54^\circ 44'$  it is thus possible to combine uniformity and intensity of the field. For  $\alpha = 63^\circ 26'$  the same value is obtained for  $\beta$  and we have the ordinary non-protruding truncated cones. These results, somewhat at variance with current ideas, were shown to be correct by measurements with a very small test-coil, for which I am indebted to Dr. W. J. DE HAAS.

For excentric axial points, at a distance  $x$  from the centre  $A$ , the value of the first term is

$$\mathfrak{H}_1(x) = 4\pi\mathfrak{J} \left( 1 - \frac{a+x}{2\sqrt{(a+x)^2 + b^2}} - \frac{a-x}{2\sqrt{(a-x)^2 + b^2}} \right) \cdot \cdot \quad (4)$$

That of the second term for one single cone

$$\begin{aligned} \mathfrak{H}_2(x) = 2\pi\mathfrak{J} \sin^2 \alpha \cos \alpha \left[ \log \frac{B-x \sin \alpha \cos \alpha + \sqrt{B^2 - 2Bx \sin \alpha \cos \alpha + x^2 \sin^2 \alpha}}{b-x \sin \alpha \cos \alpha + \sqrt{b^2 - 2bx \sin \alpha \cos \alpha + x^2 \sin^2 \alpha}} + \right. \\ \left. + \frac{x \operatorname{tg} \alpha - 2B}{\sqrt{B^2 - 2Bx \sin \alpha \cos \alpha + x^2 \sin^2 \alpha}} - \frac{x \operatorname{tg} \alpha - 2b}{\sqrt{b^2 - 2bx \sin \alpha \cos \alpha + x^2 \sin^2 \alpha}} \right] \cdot \quad (5) \end{aligned}$$

This formula was developed by CZERMAK and HAUSMANINGER in a somewhat different form.

By (4) and (5) the total field for any axial point may be calculated, whether the vertices coincide or not. However a cone is a magnetic "optimum-surface" relatively to its vertex only.

For excentric points on an equatorial  $y$ -axis the first term becomes

$$\mathfrak{H}_1(y) = 2\mathfrak{J} \int_0^{2\pi} d\theta \left[ \frac{a(ry \cos \theta - a^2 - y^2)}{(a^2 + y^2 \sin^2 \theta) \sqrt{a^2 + y^2 - 2ry \cos \theta + r^2}} \right]_{r=0}^{r=b}, \quad (6)$$

which is reducible to elliptic integrals. For the second term a still more complicated integral is found, of which the first part also leads to elliptic integrals of the third kind; whereas the logarithmic term can only be expressed by series of elliptic integrals, a result kindly worked out by Prof. W. KAPTEYN. In fact for two concentric cones we find

$$\begin{aligned}
\mathfrak{H}_2(y) = & \mathfrak{J} \sin^2 \alpha \cos \alpha \int_0^{2\pi} d\theta \left[ 2 \frac{b + (y - 2b \cos \theta) \sin^2 \alpha \cos \theta}{(1 - \sin^2 \alpha \cos^2 \theta) \sqrt{b^2 - 2by \sin^2 \alpha \cos \theta + y^2 \sin^2 \alpha}} \right. \\
& - 2 \frac{B + (y - 2B \cos \theta) \sin^2 \alpha \cos \theta}{(1 - \sin^2 \alpha \cos^2 \theta) \sqrt{B^2 - 2By \sin^2 \alpha \cos \theta + y^2 \sin^2 \alpha}} + \\
& + \log \frac{B - y \sin^2 \alpha \cos \theta + \sqrt{B^2 - 2By \sin^2 \alpha \cos \theta + y^2 \sin^2 \alpha}}{b - y \sin^2 \alpha \cos \theta + \sqrt{b^2 - 2by \sin^2 \alpha \cos \theta + y^2 \sin^2 \alpha}} \times \\
& \left. \times \frac{b - y \sin^2 \alpha \cos \theta - \sqrt{b^2 - 2by \sin^2 \alpha \cos \theta + y^2 \sin^2 \alpha}}{B - y \sin^2 \alpha \cos \theta - \sqrt{B^2 - 2By \sin^2 \alpha \cos \theta + y^2 \sin^2 \alpha}} \right] \quad (7)
\end{aligned}$$

If the point considered neither lies on the  $x$ -axis nor on the  $y$ -axis the equation for  $\mathfrak{H}_2(x, y)$  becomes more complicated still.

By applying (4) to pole-shoes having parallel frontal planes only the field for any axial point is easily found; after integration and division by the polar distance the mean value is found to be

$$\overline{\mathfrak{H}_1} = 4\pi \mathfrak{J} \left( 1 + \frac{1}{2} \frac{b}{a} - \frac{1}{2} \sqrt{4 + \frac{b^2}{a^2}} \right) \dots \quad (8)$$

As a matter of fact the uniformity in such cases is generally rather satisfactory. It may even be improved within a larger range by hollowing out the front surfaces. If a spherical zone be considered of radius  $R$ , perforated in its centre; if the visual angle of the periphery be  $2\gamma$ , that of the aperture  $2\gamma'$  as seen from the sphere's centre, then at a distance  $x$  from the latter the field is

$$\mathfrak{H} = \frac{2\pi \mathfrak{J}}{3x^3} \left| \frac{x^4 - 2R^4 + (2R^2 - x^2)Rx \cos \theta + R^2 x^2 \sin^2 \theta}{\pm \sqrt{x^2 + R^2 - 2xR \cos \theta}} \right|_{\theta=\gamma'}^{\theta=\gamma} \dots \quad (9)$$

The sign depends upon whether the point considered lies on the concave or convex side ( $x < R$  or  $> R$ ). By (9) the field in any axial point of a centered pair of spherical zones may be calculated, the interstic space having the shape of a biconvex, biconcave or concave-convex lense; without aperture we have  $\gamma' = 0$ . The formula for  $\partial^2 \mathfrak{H} / \partial x^2$  becomes rather complicated; this derivative vanishes for concentric concave hemispheres, for which we find after considerable simplification

$$\mathfrak{H} = \frac{4\pi}{3} \mathfrak{J}, \dots \dots \dots \quad (10)$$

independent of  $x$ , i. e. a perfectly uniform field, a result following moreover from known properties. The same holds more generally for a spheroidal cavity in the midst of a ferromagnetic medium, rigidly magnetised parallel to the axis of symmetry; we then have

$$\mathfrak{H} = \frac{4\pi\mathfrak{J}}{1-m^2} \left( 1 - \frac{m}{\sqrt{1-m^2}} \cos^{-1} m \right); \quad \dots \quad (11)$$

here  $m$  denotes the ratio of the axis of revolution to a transverse axis of the spheroid; such a case might be approximately realized if the necessity arose.

The attraction exerted upon a small body in an axial point is proportional to  $\partial\mathfrak{H}/\partial x$  in case of saturation, or to  $\mathfrak{J} \cdot \partial\mathfrak{H}/\partial x$  if a magnetisation proportional to the field be induced in it. It may therefore be found by differentiation of the expressions (4), (5) or (9), though this generally becomes rather intricate.

*Prismatic armatures.* If we denote the length at right angles to the normal section (Fig. 1) by  $2c$ , then we have for  $c = \infty$ , i. e. practically for prisms of sufficient length, if the inclined planes have one mutual bisectrix through  $A$

$$\mathfrak{H}^0 = \mathfrak{H}_1 + \mathfrak{H}_2 = 8\mathfrak{J}\beta + 8\mathfrak{J} \sin \alpha \cos \alpha \log \frac{B}{b} \quad \dots \quad (I^*)$$

For shorter prisms the first term becomes

$$\mathfrak{H}_1 = 8\mathfrak{J} \tan^{-1} \frac{b}{a} \sqrt{\frac{c^2}{a^2 + b^2 + c^2}}; \quad \dots \quad (I^*, 1)$$

and the second term

$$\mathfrak{H}_2 = 8\mathfrak{J} \sin \alpha \cos \alpha \left[ \log \frac{B}{b} - \log \frac{B^2 \left( \sqrt{1 + \frac{b^2}{c^2 \sin^2 \alpha}} - 1 \right)}{b^2 \left( \sqrt{1 + \frac{B^2}{c^2 \sin^2 \alpha}} - 1 \right)} \right] \quad \dots \quad (I^*, 2)$$

The subtractive term in brackets vanishes for  $c = \infty$ ; then evidently  $\partial\mathfrak{H}_2/\partial\alpha$  vanishes for  $\alpha = 45^\circ$ , which is the most favourable angle in this case, giving the strongest field; for shorter prisms however  $\alpha > 45^\circ$ .

The uniformity along the  $z$ -axis is complete for prisms of sufficient length, i. e.  $\partial^2\mathfrak{H}_x/\partial z^2 = 0$ ; for this case we find

$$\frac{\partial^2\mathfrak{H}_1}{\partial x^2} = -\frac{\partial^2\mathfrak{H}_1}{\partial y^2} = 8\mathfrak{J} \frac{\sin 2\beta \cos^2 \beta}{a^2} = 8\mathfrak{J} \frac{\sin^2 \beta \sin 2\beta}{b^2} \quad \dots \quad (1^*)$$

This expression remains positive and passes through a maximum for  $\beta = \tan^{-1} \sqrt{1/3} = 30^\circ$ , the non-uniformity consequently being greatest for this angle.

The term  $\mathfrak{H}_2$  again behaves inversely, its second derivative vanishing for this same angle; in fact  $\cos 3\alpha$  then vanishes in the formula

$$\frac{\partial^2 \mathfrak{H}_2}{\partial x^2} = -\frac{\partial^2 \mathfrak{H}_2}{\partial y^2} = 8\mathfrak{J} \sin^3 \alpha \cos 3\alpha \left( \frac{1}{b^2} - \frac{1}{B^2} \right) \dots \dots (2^*)$$

As  $B > b$  this expression is  $\pm$  for  $\alpha \lesseqgtr 30^\circ$ . For the total field we finally have

$$\frac{\partial^2 (\mathfrak{H}_1 + \mathfrak{H}_2)}{\partial x^2} = 8\mathfrak{J} \frac{1}{b^2} \left[ \sin^2 \beta \sin 2\beta + \sin^3 \alpha \cos 3\alpha \left( 1 - \frac{b^2}{B^2} \right) \right] \dots (3^*)$$

Equalizing the bracketed terms to zero gives a relation between  $\alpha$  and  $\beta$ ; neglecting  $b^2/B^2$  we find

e.g. for	$\alpha = 30^\circ$	$45^\circ$	$48^\circ$	$50^\circ 46'$	$54^\circ 44'$	$60^\circ$
the value:	$\beta = 90^\circ$	$82^\circ 38'$	$79^\circ 59'$	$77^\circ 9'$	$72^\circ 26'$	$60^\circ$

as corresponding sets. For  $\alpha = 60^\circ$  we obtain the same value for  $\beta$ , i. e. non-protruding frontal rectangles.

In excentric axial points at a distance  $x$  from the centre  $A$  the value of the first term is

$$\mathfrak{H}_1(x) = 4\mathfrak{J} \tan^{-1} \frac{2ab}{a^2 - b^2 - x^2} \dots \dots \dots (4^*)$$

That of the second term for one pair of inclined planes

$$\left. \begin{aligned} \mathfrak{H}_2(x) = 2\mathfrak{J} \sin \alpha \cos \alpha \left[ \log \frac{B^2 - 2Bx \sin \alpha \cos \alpha + x^2 \sin^2 \alpha}{b^2 - 2bx \sin \alpha \cos \alpha + x^2 \sin^2 \alpha} + \right. \\ \left. + 2 \operatorname{tg} \alpha \left( \tan^{-1} \frac{b - x \sin \alpha \cos \alpha}{x \sin^2 \alpha} - \tan^{-1} \frac{B - x \sin \alpha \cos \alpha}{x \sin^2 \alpha} \right) \right] \end{aligned} \right\} (5^*)$$

By means of (4\*) and (5\*) the total field may be calculated for any axial point, whether the 4 inclined planes intersect in one line or not; only in the former case do they form an "optimum-surface" with regard to  $A$ .

For excentric points on an equatorial axis of  $y$  we find as the first term, for  $c = \infty$

$$\mathfrak{H}_1(y) = 4\mathfrak{J} \tan^{-1} \frac{2ab}{a^2 - b^2 + y^2}; \dots \dots \dots (6^*)$$

and as the second term for two pairs of inclined planes

$$\left. \begin{aligned} \mathfrak{H}_2(y) = 2\mathfrak{J} \sin \alpha \cos \alpha \left[ \log \frac{B^2 + 2By \sin^2 \alpha + y^2 \sin^2 \alpha}{b^2 + 2by \sin^2 \alpha + y^2 \sin^2 \alpha} \times \right. \\ \times \frac{B^2 - 2By \sin^2 \alpha + y^2 \sin^2 \alpha}{b^2 - 2by \sin^2 \alpha + y^2 \sin^2 \alpha} + 2 \operatorname{tg} \alpha \left( \tan^{-1} \frac{y \sin^2 \alpha + b}{y \sin \alpha \cos \alpha} + \right. \\ \left. + \tan^{-1} \frac{y \sin^2 \alpha - b}{y \sin \alpha \cos \alpha} - \tan^{-1} \frac{y \sin^2 \alpha + B}{y \sin \alpha \cos \alpha} - \tan^{-1} \frac{y \sin^2 \alpha - B}{y \sin \alpha \cos \alpha} \right) \left. \right] \end{aligned} \right\} (7^*)$$

The distribution of the field is thereby completely determined; in

the symmetric equatorial plane it is everywhere directed parallel to the  $x$ -axis. The most general case of any arbitrary point in the field leads to an expression for  $\mathfrak{H}_2(x, y)$ , capable of integration but more complicated still than (7\*). By differentiation  $\partial\mathfrak{H}_x/\partial y$  may also be obtained, though this also turns out rather intricate. In much the same way the distribution of  $\mathfrak{H}_x$  along the  $z$ -axis may be calculated for prisms of finite length and the integrals.

$$\int_{z_1}^{z_2} \mathfrak{H}_x(z) dz \quad \text{and} \quad \int_{z_1}^{z_2} \mathfrak{H}_x^2(z) dz$$

may be computed, of which the latter is of importance e. g. in the study of transverse magnetic birefringency. The case of an air-space shaped like a cylindric lens is of less practical importance and may here be omitted.

**Physiology.** — *“Influence of some inorganic salts on the action of the lipase of the pancreas.”* (By Prof. Dr. C. A. PEKELHARING.)

Hydrolytic fat-splitting by the lipase of the pancreas, the only enzyme that will be considered here, may be aided by a number of inorganic salts as well as by bile acids. It does not follow however that this action is always due to the same cause, to the process of activating the enzyme.

It has been proved by RACHFORD as early as 1891 that bile aids the action of the lipase of the pancreas especially on account of the presence of bile salts. The fat-splitting power of rabbit's pancreatic juice was increased by the addition of a solution of glycocholate of soda nearly as much as by the addition of bile <sup>1)</sup>. According to the researches of more recent investigators, especially TERROINE <sup>2)</sup>, it is highly probable, that the action of bile acids is based on a direct influence on the enzyme, so that here we might speak of an “activator” in the real sense of the word. The fact that various electrolytes also aid the hydrolysis of fat by the lipase, has been demonstrated by POTTEVIN <sup>3)</sup> and more in detail by TERROINE <sup>4)</sup>; afterwards also by MINAMI <sup>5)</sup>. However, the mode of action of the electrolytes is still unknown, as has been clearly pointed out by TERROINE. The investigators I mentioned used for their experiments pancreatic juice or a

<sup>1)</sup> Journ. of Physiol. Vol. XII. p. 88.

<sup>2)</sup> Biochem. Zeitschr. Bd. XXIII. S. 457.

<sup>3)</sup> Compt. rend. Acad. d. Sciences, T. CXXXVI, p. 767.

<sup>4)</sup> l. c. S. 440.

<sup>5)</sup> Bioch. Zeitschr. Bd. XXXIX, S. 392.



glycerin extract of the pancreas, liquids containing, besides lipase, a great quantity of other substances, chiefly proteins, and moreover some electrolytes. TERROINE has tried to remove the electrolytes from the pancreatic juice by dialysis, but this did not bring him nearer to his end, the dialysis causing the juice to lose its lipolytic activity.

ROSENHEIM has discovered<sup>1)</sup>, that this was not due to deleterious action on the enzyme by the dialysis, nor to the diffusion of the lipase through the wall of the dialyser, but to the removal of a co-enzyme that readily diffuses, that withstands boiling and is soluble in alcohol.

If the diffusate is evaporated and again added to the contents of the dialyser, its fat-splitting power is as great as before. The co-enzyme can be separated from the lipase not only by dialysis but also, as ROSENHEIM demonstrated, by diluting the glycerin extract of the pancreas with water, the result being a precipitate containing the enzyme, while the co-enzyme is left behind in solution.

ROSENHEIM's suggestions induced me to use for my experiments lipase prepared in the following way:

Fresh pig's pancreas was minced up, then mixed with about twice its weight of glycerin and percolated after 24 hours. By filtration through a compressed pulp of filterpaper a solution can be obtained that is only slightly opalescent, whose lypolitic power however is far inferior to the original extract. Besides it yields after dilution with water a much smaller quantity of precipitate containing lipase. In preparing the enzyme I therefore used the extract only percolated through fine linen. This extract is highly opalescent, but little or no precipitate settles even after standing long. Part of this, mostly 30 cc, was mixed with ten times its quantity of distilled water. The liquid is very milky; however a satisfactory precipitate is not always obtained.

To this effect a very faintly acid reaction, by addition of a few drops of diluted acetic acid, is required so as to colour sensitive blue litmuspaper faintly red. A stronger acid reaction would also cause a rather considerable amount of trypsin and trypsinogen to be precipitated. Next day the perfectly clear liquid is cautiously decanted off from the residue and exchanged for 300 cc. of water; if necessary the water is acidulated with a few drops of acetic acid. After precipitation the decantation is repeated. The remaining fluid together with the precipitate is put on hardened paper in a BUCHNER filter and filtered off under pressure. The precipitate is repeatedly

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<sup>1)</sup> Proc. Physiol. Soc. Febr. 19, 1910, Journ. of Physiol, Vol. XL.

washed in distilled water on the filter. It is then a greyish white mass which, after being thoroughly deprived of the superfluous water, can be easily removed from the filter and is now sufficiently free from electrolytes. After incineration the substance dried at 110° C.

0.1521 grm. yielded 0.0004 gr. of ash

and 0.2761 grm. yielded 0.0010 gr. of ash.

The solution of this ash in boiling hydrochloric acid was yellow, which colour disappeared on dilution with water. This solution got vividly red with potassium sulphocyanate and did not give any calcium reaction. It was evident therefore, that the ash was chiefly composed of iron phosphate, which was not present before but only formed during incineration.

The matter precipitated by dilution of the glycerin extract with water is soluble in highly dilute alkali. However, it also dissolves in glycerin without alkali. To effect this the precipitate, taken from the filter, was rubbed up in a mortar with pure glycerin. The solution gets clouded, nevertheless practically homogeneous. It preserves its activity also after standing for a long time. Filtration makes it quite clear again, but deprives it of much of its activity. That is why I used the unfiltered solution. To dissolve the precipitate from 30 cc. of pancreatic extract, 20 cc. of glycerin was used, after which process the concentration of the enzyme — considering the inevitable loss of matter — was about equal to that of the original extract. The proteolytic and the amylolytic enzymes have been all but eliminated by the washing. The glycerin solution hardly attacks boiled starch and fibrin, not even after addition of some calcium chloride. It contains however a considerable amount of lipase. Still, the action of the enzyme is extremely weak without the addition of other substances.

As ROSENHEIM detected, its activity is raised by mixing with the washwater (concentrated by evaporation), which has been separated from the precipitate, also when the evaporation occurs at a high temperature. Whereas in this respect ROSENHEIM's statements were fully confirmed by my experiments, I have been able to prove that, contrary to ROSENHEIM's results, the power to aid the lipolysis is not lost through combustion. It is necessary, however, to dissolve the ash with a small quantity of boiling hydrochloric acid. When mixed with the neutralized solution, the glycerin solution of the enzyme (which further on I shall call only "lipase") evinces intense lipolysis.

It is especially (though not exclusively) the calcium present in the ash that increases the activity of the enzyme. The bearing of very

small quantities of lime salt on the lipolysis is not hard to test: Some drops of commercial olive oil are mixed with highly diluted soda and a few drops of lipase. After thorough intermixture by which the enzyme, left in solution by the weak alkali, is equally distributed in the fluid, and after addition of a little phenolphthalein, equal portions of the emulsion are put in two tubes, after which to the one calcium is added, for instance 1 drop of  $\text{CaCl}_2$  1 % to 5 cc. of the fluid. The red colour will disappear, at least will get much fainter. Subsequently the fluid is made as red again as that of the other tube by cautious addition of sodium carbonate. When both tubes are heated to the temperature of the body, it will be seen that the one with calcium soon loses its red colour while its acidity is gradually increasing, whereas the colour of the other hardly changes or does not do so at all, in an hour's time. The reaction should be made very slightly alkaline, because the enzyme, especially at the temperature of the body is soon destroyed by alkali.

It thus appeared that, in order to confer activity on the almost inactive lipase, the only salt in it being a little sodium carbonate, we do not want the addition of the mixture of substances dissolved in water from the pancreatic extract, but that calcium chloride will do for the purpose.

For a more exact investigation of the lipolysis I proceeded as follows: 3 to 4 cc. of the lipase was mixed with about double the quantity of a 0.2 % solution of  $\text{Na}_2\text{CO}_3$  and on addition of ten drops of phenolphthalein diluted with water to 200 cc. This slightly opalescent fluid of reddish coloration was equally distributed among four bottles of 150 cc. capacity each; to each bottle 1 cc. of neutral olive oil was added, the oil being liberated from fatty acids by shaking up the ether solution with sodium hydrate. Beforehand the bottles were furnished with the substance whose action on the lipase was the object of our research. When OH-ions were fixed by the investigated matter, the pink colour was equalized in all the bottles by means of  $\text{Na}_2\text{CO}_3$ . Hereupon the well-corked bottles were put in the thermostat at  $38^\circ \text{C}$ . and turned slowly round an horizontal axis mostly for 6 hours, so as to ensure a constant regular intermixture of their contents. After 50 cc. of 92 % alcohol had been added to each bottle, the amount of acid was determined by titration with  $\frac{n}{4} \text{NaHO}$ .

It now invariably appeared, that some acid had also been set free in the bottles containing only lipase, some sodium carbonate, water and oil. The quantity varied in different preparations of the enzyme, but was the same in each preparation on different days. It can hardly

be supposed that the lipolysis, in this case, depended on bacteria and not on the lipase of the pancreas. It came forth also when 10 cc. of toluol was added to the fluid and it was arrested without toluol even when the quantity of acid was extremely small. The greatest amount of acid was in a great number of experiments found to be still less than  $\frac{1}{200}$  normal. SÖHNGEN<sup>1)</sup> found that the activity of the lipase of bacteria can be destroyed only by  $\frac{1}{50}$  *n* lactic acid.

ROSENHEIM holds that the fact that the lipase of the pancreas remains active even without addition of co-enzyme, is to be ascribed to its not being sufficiently purified. Considering that electrolytes had been all but completely removed from the lipase prepared by me, and again that the electrolytes of the pancreas (more especially the calcium salts) are alone sufficient to aid the activity of the lipase, I have tried to find another plausible explanation.

Since several observers have demonstrated that lipase, including that of the pancreas, is able not only to split fat but also to synthesize fat from fatty acid and glycerin, we may be justified in supposing that the action of this enzyme consists in favouring an equilibrium reaction, a supposition borne up by DIETZ's<sup>2)</sup> laborious investigations. Now, when the lipase decomposes oil in presence of calcium salt, it is very remarkable that, while the bottles are being turned round in the thermostat, a considerable amount of calcium soap is carried out of solution, partly as a solid precipitate lining the wall of the bottle, partly as gelatinous lumps in the liquid. It is therefore permissible to conclude, that fat-splitting is stopped as soon as a small quantity of fatty acid has been separated; again, that in consequence of this the lipolysis in the salt-free solution is indeed not wanting, but that it soon ceases; and finally, that the action of the calcium salt results in separating the fatty acid in insoluble condition, as it is set free.

The following experiments will illustrate the influence of  $\text{CaCl}_2$ .

Every bottle contained 1 cc. of lipase in 50 cc. of water with phenolphthalein and just enough soda to evolve a very light pink colour of the fluid. After six hours' shaking in the thermostat at 38° C. the following results were arrived at by titration:

I	without addition	. . . . .	0.2 cc. $\frac{n}{4}$ NaHO
	with 2 c.c. $\text{CaCl}_2$ 1%	. . . . .	1.5 ,, ,,
II	without addition	. . . . .	0.6 ,, ,,

<sup>1)</sup> Folia microbiologica. I, p. 199.

<sup>2)</sup> Zeitschr. f. Physiol. Chem. Bd. LII, S. 279.

	with 10 mgr. CaCl <sub>2</sub> .	. . . . .	1.1 cc.	$\frac{n}{4}$ NaHO
	„ 25 „ „	. . . . .	1.4 „	„
III	without addition	. . . . .	0.9 „	„
	with 10 mgr. CaCl <sub>2</sub> .	. . . . .	2.0 „	„
IV	without addition	. . . . .	0.6 „	„
	with 100 mgr. CaCl <sub>2</sub>	. . . . .	1.6 „	„
	„ 200 „ „	. . . . .	1.7 „	„
	„ 400 „ „	. . . . .	2.2 „	„

I was not astonished to find, that the lipolysis did not increase in the same degree as the amount of lime salt, nor that it did not increase regularly, since the quantity of fat contained in the gelatinous deposit of calcium soap varies and in virtue of this a varying quantity of fat is abstracted from the influence of the enzyme. The precipitate also comprises free fatty acid, as it appeared necessary during titration to shake the fluid well. Thereby the tough calcium-soap was crumbling away and passed into coarse flakes collecting, after standing a short time, on the surface of the alcoholic fluid. When the calcium soap was broken up, alkali disappeared as was evident from the disappearance of the red colour.

That Ca Cl<sub>2</sub> had indeed been decomposed by the fatty acid, may also be concluded from the greater amount of H'-ions in the fluid, the determination of which I owe to Dr. RINGER.

A solution of 4 cc. of lipase with a little sodium carbonate in 400 cc., was distributed in 4 bottles, and 1 cc. of neutral oil was added to each bottle. After digestion for 6 hours 50 cc. was pipetted off from each bottle to determine the H'-concentration. The remaining 50 cc. containing about all the calcium soap was titrated.

<i>a</i>	without addition,	0.6 cc.	$\frac{n}{4}$ NaHO,	$c_H 8.1 \times 10^{-8}$
<i>b</i>	with 10 mgr. CaCl <sub>2</sub>	1.0 „	„	$c_H 6.6 \times 10^{-7}$
<i>c</i>	„ 25 „ „	1.4 „	„	
<i>d</i>	„ 50 „ „	1.6 „	„	$c_H 2.6 \times 10^{-6}$

The apparatus only allowed to work with three H-electrodes at a time, so that no H'-determination was made of *c*.

Though the greater part of the titratable acid was left in the bottles, acidity, increasing with the amount of CaCl<sub>2</sub>, was distinctly noticeable in the fluid pipetted from *b* and *d*. Thus the fluid contained a strongly dissociated acid, which in this case was sure to be hydrochloric acid.

The lipolysis is also aided by lime salts that are very difficult to dissolve.

4 cc. of lipase, after addition of 6 cc. of  $\text{Na}_2\text{CO}_3$  0.2 %, diluted with water to 200 cc., is distributed in 4 bottles. To *a* only 1 cc. of neutral oil was added. To *b* moreover, 2 cc. of  $\text{CaCl}_2$  1%, to *c* 2 cc. of  $\text{CaCl}_2$  1% as well as 3 cc. of an equivalent solution of  $\text{K}_2\text{C}_2\text{O}_4$  and to *d* the centrifugalised washed precipitate obtained by mixing 2 cc. of  $\text{CaCl}_2$  1% with 3 cc. of the same solution of calcium oxalate. After digestion for six hours I found:

<i>a</i>	uses	0.2 cc.	$\frac{n}{4}$	NaHO
<i>b</i>	„	2.0	„	„
<i>c</i>	„	0.9	„	„
<i>d</i>	„	1.0	„	„

Calcium carbonate works likewise. The experiment also showed that  $\text{CO}_2$  was set free.

200 cc. solution of 4 cc. of lipase, with a little soda in 4 bottles *a*, *b*, *c*, and *d* 50 cc. each. Beforehand I had put in *c* and *d*  $\pm$  200 mgr. of freshly precipitated  $\text{CaCO}_3$  which was obtained by precipitating a water solution of 300 mgr. of  $\text{CaCl}_2$  with  $\text{Na}_2\text{CO}_3$  and repeatedly washing the precipitate with water in a centrifuge.

The fluids, each with 1 cc. of oil, were digested for six hours. Immediately after this *a* and *c* were titrated. Through *b* and *d* a current of air free of  $\text{CO}_2$  at  $25^\circ\text{C}$ . was passed for an hour and carried off through 50 cc. n/50 of barytic water. Subsequently also *b* and *d* were titrated. The barytic water through which the air in *d* was carried off had got very turbid, that of *b* hardly clouded. After precipitation of the barium carbonate formed, 40 cc. of the limpid fluid from each bottle was titrated with n/5 HCl. The result was:

<i>a</i>	uses	0.6 cc.	$\frac{n}{4}$	NaHO
<i>b</i>	„	0.6	„	„ and yields 0,14 cc. $\frac{n}{4}$ $\text{CO}_2$
<i>c</i>	„	4.2	„	„
<i>d</i>	„	3.7	„	„ „ 1.18 „ „

A rather considerable quantity of carbonic acid had therefore been liberated from the calcium carbonate. The total acidity of *d* was 4.88, that of *c* being 4.2. Though, in the titration of the digested cloudy fluid, errors of 0.1, nay even of 0.2 cc. may possibly occur, this difference lies beyond the limit of the errors. The reason is obvious. While the air passed through the liquid it was heated to  $25^\circ\text{C}$ . to

drive off the carbonic acid. Consequently the lipolysis could proceed again for the very reason, that by expelling the carbonic acid the equilibrium in the fluid was disturbed. Fatty acid could now be precipitated again through presence of the excess of calcium carbonate.

As regards the action of calcium salts my results are not quite the same as those of TERROINE, who found no or hardly any increase of the lipolysis by calcium chloride. The nature of TERROINE's experiments however differed from mine. This experimenter made use of dog's pancreatic juice of which 5 cc. was digested with 5 cc. of olive oil. This mixture, even without any addition, contained lime, and besides other electrolytes, a large quantity of colloid substances and comparatively little water, whereas for my researches the lipase, as much as possible freed from the other constituents of the pancreatic extract, especially from the electrolytes, was dissolved in glycerin and strongly diluted with water. This method enabled me to study the action of the electrolytes all the better.

Indeed, TERROINE found the lipolysis increased after addition of magnesium- and barium chloride. This supports the belief that the action of the enzyme is promoted by precipitation of the liberated fatty acid. In this respect my results agreed with TERROINE's as may appear from the following instances:

Again 4 cc. of lipase was dissolved with a little sodium carbonate in water to a volume of 200 cc. and divided into four equal portions of 50 cc. To three of them equivalent quantities of  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ , or  $\text{MgCl}_2$  were added. The faint pink colour which disappeared, returned after the addition of some soda.

After six hours' digestion I used:

I	without addition	. . . . .	0.6 cc.	$\frac{n}{4}$	NaHO
	with 100 mgr. $\text{CaCl}_2$	. . . . .	1.4	„	„
	„ 220 „ $\text{BaCl}_2$	. . . . .	1.3	„	„
	„ 185 „ $\text{MgCl}_2$	. . . . .	2.7	„	„
II	without addition	. . . . .	0.5	„	„
	with 200 mgr. $\text{CaCl}_2$	. . . . .	2.0	„	„
	„ 440 „ $\text{BaCl}_2$	. . . . .	1.6	„	„
	„ 370 „ $\text{MgCl}_2$	. . . . .	3.7	„	„
III	without addition	. . . . .	0.5	„	„
	with 100 mgr. $\text{CaCl}_2$	. . . . .	0.9	„	„
	„ 220 „ $\text{BaCl}_2$	. . . . .	1.1	„	„
	„ 185 „ $\text{MgCl}_2$	. . . . .	2.5	„	„

The magnesium soap which was formed, was not so tough and gelatinous as the calcium and the barium soap and could therefore not take up so much of the oil. Consequently less oil was protected against the action of the enzyme. I think the more powerful action of the magnesium chloride is owing to this fact.

As known, sodium salts also aid the lipolysis. Here also, I think, the action is caused by the separation of fatty acid from the fluid, as insoluble soap. Sodium oleate is precipitated by solutions of different sodium salts of sufficient concentration, whereas in very weak salt solutions as well as in water they dissolve with opalescence.

In order to arrive at an approximate estimation as to the degree of solubility, I made a solution of sodium oleate by dissolving pure oleic acid in alcohol and adding to it sufficient sodium hydrate to produce distinct alkaline reaction. Several mixtures were made of 5 drops of this solution with 20 cc. of salt solutions varying in strength. This mixture was at once filtered. The filtrate was found to be less cloudy according as the precipitation had been more complete.

NaCl	4%	. . . . .	filtrate clear
„	2%	. . . . .	„ slightly opalescent
NaBr	6%	. . . . .	„ clear
„	4%	. . . . .	„ slightly opalescent
„	2%	. . . . .	„ cloudy
NaI	7.6%	. . . . .	„ clear
„	3.8%	. . . . .	„ cloudy
NaF	3%	. . . . .	„ clear.
„	1.5%	. . . . .	„ cloudy
CaCl <sub>2</sub>	0.2%	. . . . .	„ clear
„	0.1%	. . . . .	„ clear
„	0.05%	. . . . .	„ very cloudy
MgCl <sub>2</sub>	0.4%	. . . . .	„ clear
„	0.2%	. . . . .	„ clear
„	0.1%	. . . . .	„ clear
KCl	4%	. . . . .	„ cloudy
„	2%	. . . . .	„ very cloudy

By these researches the positive bearing of these salts (except that of NaI and NaF) on the lipolysis was ascertained. KCl, which does not precipitate soap by far so well as sodium salts, also exerted much less influence upon the lipolysis. The experiments were made in the usual way. Every time 50 cc. of a lipase and oil mixture, with or without addition of salt was digested for 6 hours and subsequently titrated. I used:



I	without addition . . . . .	0.8 cc. $\frac{n}{4}$ NaHO
	with 2 gram. NaCl. . . . .	2.4 " "
	" 4 " " . . . . .	4.6 " "
	" 6 " " . . . . .	4.4 " "
II	without addition . . . . .	0.8 " "
	with 2 gram. KCl . . . . .	0.5 " "
	" 4 " " . . . . .	1.3 " "
	" 6 " " . . . . .	2.0 " "
III	without addition . . . . .	0.5 " "
	with 2 gram. NaCl . . . . .	1.3 " "
	" 6 " NaBr . . . . .	1.6 " "
	" 7.6 " NaI . . . . .	0.9 " "
IV	without addition . . . . .	0.5 " "
	with 3 gram. NaCl . . . . .	2.3 " "
	" 9 " NaBr . . . . .	3.5 " "
	" 11.4 " NaI . . . . .	0.8 " "

When the fluid contained NaI it got slightly yellow during digestion. That the lipolysis was very insignificant every time was no doubt owing to the liberation of iodine. NaF, indeed, aided fat-splitting in some degree, but much less than NaCl and NaBr.

The above experiments led to the conclusion, that the electrolytes under investigation did not aid the lipolysis by conferring activity on the enzyme itself, but by neutralizing one of the products of the splitting, viz. fatty acids.

I have tried to test this also in another manner. An activator of the lipase, in the real sense of the word, may be expected to exert its influence as well in the synthesis of fat from fatty acid and glycerin as in fat splitting. Such indeed is the case with respect to bile acids as HAMSİK has demonstrated<sup>1)</sup>. If however the action of electrolytes consists only in the precipitation of soap, they cannot promote the synthesis, a counteraction is rather to be expected.

I proceeded as follows :

Glycerin was digested with oleic acid and lipase in the thermostat at 38° C., while being shaken slowly but incessantly. Toluol was added because the experiments generally lasted 24 hours or even longer. Originally I tried to determine the acidity of the fluid at the beginning of the experiment, by titrating a measured portion of it directly after mixing.

However, serious errors ensued, because of the impossibility to

<sup>1)</sup> Zeitschr. f. Physiol. Chem. Bd. LXV, S. 232.

keep the fluid well mixed during the pipetting even after shaking it thoroughly. Therefore mixtures of oleic acid and glycerin of the same composition as those that were to be digested, were prepared separately and immediately after the acidity was determined by titration. These samples were taken in duplicate in order to discover eventual errors in the measuring of the oleic acid.

In every experiment I used: 10 cc. of glycerin, 2 cc. of oleic acid, 2 cc. of lipase and 3 cc. of toluol with or without addition of salt. The following are some of the results obtained:

		cc. $\frac{n}{4}$ NaHO		
Addition		Immediately.	After 24 hours.	After 48 hours.
I.	0	{ 23.9 23.6	17.2	13.9
	200 mgr. CaCl <sub>2</sub>		23.1	23.4
II.	0	{ 23.0 23.5	18	19.5
	100 mgr. CaCl <sub>2</sub>		23.3	23.0
Addition.		Immediately.	After 24 hours	
III.	0	{ 23.5 23.6	16.9	
	10 mgr. CaCl <sub>2</sub>		19.3	
	30 „ „	20.4		
	50 „ „	22.1		
IV.	0	{ 23.6 23.6	17.2	
	10 mgr. BrCl <sub>2</sub>		18.8	
	50 „ „	22.0		
	100 „ „	23.7		

It is evident therefore that the synthesis was not increased. It was even strongly inhibited, just the reverse result as was obtained after addition of bile salts, prepared from oxbile after PLATTNER'S method.

		cc. $\frac{n}{4}$ NaHO			
Addition.		Immediately.	After 10 hrs.	After 24 hrs.	After 48 hrs.
I.	0	{ 23.3 23.6		15.1	14.9
	100 mgr. bilesalts			10.4	9.5
II.	0	{ 23.2 23.5	19.8	16.7	
	100 mgr. bilesalts.		14.2	11.2	

It cannot be doubted therefore, that with regard to the activity of the lipase calcium-, barium-, magnesium- and soda salts play a part totally different from that of bile acids. It seems to me that from the above the conclusion may be drawn, that the said salts separate fatty acid from the solution as soap, and for that reason increase the fat-splitting power of the enzyme.

**Geology.**—“*On rhyolite of the Pelapis Islands.*” By Prof. A. WICHMANN.

The Pelapis Islands rise between the Westcoast of Borneo and the Karimata Islands about  $1^{\circ}17' S.$   $109^{\circ}10' E.$  and consist, besides a few small islets, of the four high uninhabited and not easily accessible islands 1<sup>st</sup> Pelapis Tiang Balei, also called Pelapis Hangu, or Pelapis Ajer Tiris, 2<sup>nd</sup> Pelapis Rambai or Pelapis Ajer Masin, 3<sup>rd</sup> Pelapis Genting and 4<sup>th</sup> Pelapis Tekik <sup>1)</sup>. They reach a height of 359 m. <sup>2)</sup>. Their total surface amounts to about 13 km<sup>2</sup>.

The group of islands was visited in 1854 by the mining-engineer R. EVERWIJN, who communicates the following particulars about their geological condition.

“In the Pelapis or Melapis Islands both neptunian and plutonic formations are found. The former are clay-rocks which are so much metamorphosed by granite and a rock analogous to syenite that it is often difficult to recognize its original character. In these islands plutonic rocks contain a small quantity of magnetic iron-ore and hematite <sup>3)</sup>.”

The Mineralogical and Geological Institution at Utrecht received in 1895 among others through the kindness of the Royal Physical Society (Kon. Natuurk. Vereeniging at Batavia) as a present a specimen of the metamorphosed clay-rocks collected by EVERWIJN <sup>4)</sup>.”

<sup>1)</sup> J. P. J. BARTH. Overzicht der afdeeling Soekadana. Verhandel. Batav. Genootschap van K. en W. L. 2. Batavia 1897, p. 61.

<sup>2)</sup> M. C. VAN DOORN. Verslag omtrent de opname van Straat Karimata. Meded. betr. het Zeewezen XXIII. 2. 's-Gravenhage 1882, p. 12. — Gids voor het bevaren van Straat Karimata. Batavia 1884, p. 31.

<sup>3)</sup> Onderzoek naar tinerts in de landschappen Soekadana, Simpang en Matan en naar antimoniumerts op de Karimata-eilanden. Natuurk Tijdschr. Ned. Ind. IX. Batavia 1855, p. 63. Reprinted with map in the Jaarboek van het Mijnwezen N. O. Indië. Amsterdam 1879. I, p. 64.

<sup>4)</sup> As EVERWIJN mentions nowhere (not even on the label) on which island he has collected the above-mentioned rock, we give here a statement of the geological condition of the islands according to his map:

It appeared immediately that the above-mentioned specimen has nothing to do with clay-slate, but is a genuine eruptive-rock showing excellent *piperno*-structure. The dark brownish-red faint colour of the chief mass seems to have given rise to EVERWIJN'S error. Characteristic are the numerous lens- or disk-shaped "Schlieren" ending in a point, which, being arranged more or less parallel, contrast sharply with the groundmass. The specimen is distinguished from the typical piperno by the much more intimate connection between "Schlieren" and groundmass, and by its inferior porosity.

The analysis of the rock (I), for which I am indebted to Prof. Dr. M. DITTRICH of Heidelberg gave the following result:

	I	II
Si O <sup>2</sup> . . . . .	67,37 . . . . .	69,04
Ti O <sup>2</sup> . . . . .	0,69 . . . . .	—
Al <sup>2</sup> O <sup>3</sup> . . . . .	12,53 . . . . .	} 17,09
Fe <sup>3</sup> O <sup>3</sup> . . . . .	6,37 . . . . .	
Fe O . . . . .	0,49 . . . . .	—
Mn O . . . . .	trace . . . . .	—
Ca O . . . . .	trace . . . . .	0,74
Mg O . . . . .	0,97 . . . . .	trace
K <sup>2</sup> O . . . . .	10,01 . . . . .	9,74
Na <sup>2</sup> O . . . . .	0,03 . . . . .	2,34
CO <sup>2</sup> . . . . .	trace . . . . .	—
H <sup>2</sup> O {	under 110° . . . . . 0,56	} loss of incandesc. 0,94
{	over 110° . . . . . 1,36	
	100,38	99,89

From this analysis it appears that among all the rocks that have hitherto been found in the Indian Archipelago, the above-mentioned eruptive rock is richest in potash. From the — alas incomplete — analysis II communicated at the same time<sup>1)</sup> appears further its

Pelapis Tiang Balei	granite and in the N.W. part	clay-rocks
Pelapis Genting	" " " " N.	" "
Pelapis Rambai	" " " " N.E.	" "
Pelapis Tekik (Pelapis Tukang Kluwar)	" " " " N.W. half	" "
Pelapis Suka	"	
Pulu Dua and Pulu Bulak	clay-rocks.	

This does not imply, of course, that all that was called by EVERWIJN clay-slate, should be classed with the rhyolitic rocks.

<sup>1)</sup> CARL VON HAUER. Rhyolith aus dem Eisenbacher Thal. Verhandl. k. k. geolog. Reichsanst. Wien. 1868, p. 386.

close affinity with the rhyolite of EISENBACH near Vichaye<sup>1)</sup> in Hungary.

According to the method of W. CROSS, J. P. IDDINGS, L. V. PIRSSON and H. S. WASHINGTON<sup>2)</sup> the calculation of the mineralogical composition gave the following result:

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	
Orthoclase	38.88	—	11.02	—	—	—	10.17	—	60.07
Albite	0.17	—	0.05	—	—	—	—	0.03	0.25
Corundum	—	—	1.65	—	—	—	—	—	1.65
Ilmenite	—	0.70	—	—	0.31	—	—	—	1.01
Hematite	—	—	—	6.47	—	—	—	—	6.47
Hypersthene	1.68	—	—	—	0.19	0.99	—	—	2.86
Quartz	27.69	—	—	—	—	—	—	—	27.69
	68.42	0.70	12.72	6.47	0.50	0.99	10.17	0.03	100.00

	salic :	femic :
Orthoclase	60.07	Ilmenite 1.01
Albite	0.25	Hematite 6.47
Corundum	1.65	Hypersthene 2.86
Quartz	27.69	
	89.66	10.34

To the rock in the chemical system consequently a place must be assigned in:

$$\frac{\text{Sel}}{\text{Fem}} = \frac{89.66}{10.34} > \frac{7}{1} \dots = \text{Class I. Persalane.}$$

$$\frac{\text{QFL}}{\text{CZ}} > \frac{7}{1} \dots = \text{Subclass I. Persalone.}$$

$$\frac{\text{Q}}{\text{F}} = \frac{27.69}{60.32} < \frac{3}{5} > \frac{1}{7} \dots = \text{Order 4. Britamare.}$$

$$\frac{\text{K}^2\text{O} + \text{Na}^2\text{O}}{\text{CaO}} > \frac{7}{1} = \frac{88.01}{\text{trace}} = \text{Rang I. Liparose.}$$

<sup>1)</sup> Not Vichnye, as J. ROTH (Beiträge zur Petrographie der plutonischen Gesteine. Abhdlg. k. Akad. d. W. 1869. II. Berlin 1870, p. LXXXIII) and all those who copied him, communicate.

<sup>2)</sup> Quantitative Classification of Igneous Rocks. Chicago 1903, p. 110 et seq.

$$\frac{\text{K}^2\text{O}}{\text{Na}^2\text{O}} = \frac{10.17}{0.03} < \frac{7}{1} \dots = \text{Subrang 1. Lebachose.}$$

Although the analysis points to a rather high percentage of quartz the  $\text{SiO}_2$  percentage is rather low for a rhyolite, it approaches already more that of trachytes. With regard to this fact and taking into consideration the high percentage of  $\text{Fe}_2\text{O}_3$ , the specific weight is very high for a rhyolite namely 2.623.

It cannot be said that there is a similarity of any significance between the real mineralogical composition and the one calculated from the analysis. For this too few individuals have separated from the magma. So we discover under the microscope only a very slight quantity of more or less rectangular sanidine-plates, besides very few lath-shaped plagioclases, and likewise very rarely some augite-crystals. The groundmass is amorphous, chiefly microfelsitic. On the spots where it has become crystalline no distinguishable constituents occur. Occasionally spherulitic formations are detected. It is however very rich in ore-particles, by far the greater quantity of these should be classed with hematite, though they are only exceptionally plate-shaped. As a rule one discerns only black and irregularly shaped particles, and it is these that accumulate in the "Schlieren" and make them appear black at first sight. Besides this difference which has already come off at the differentiation of the magma the main mass of the rock does not vary in the least from the "Schlieren". E. KALKOWSKY when examining the genuine piperno which in a mineralogical and chemical respect differs so much from the rock originating from the Pelapis Islands, had already come to the same result.<sup>1)</sup>

"Wer könnte an der Lavennatur des sonderbaren Piperno zweifeln?" once exclaimed LEOP. VON BUCH.<sup>2)</sup> He was mistaken, for at all events during the last decenniums objections have been made against this view. Besides A. SCACCHI<sup>3)</sup>, LUIGI DELL'ERBA<sup>4)</sup>, P. FRANCO<sup>5)</sup>, especially

<sup>1)</sup> Ueber den Piperno. Zeitschr. d. Deutschen geolog. Gesellsch. XXX. Berlin 1878, p. 673.

<sup>2)</sup> Geognost. Beobachtungen auf Reisen. II. Berlin 1809, p. 209, reprinted in Gesammelte Werke I. Berlin 1867, blz. 459.

<sup>3)</sup> This was still his opinion in 1849. Afterwards he regarded the piperno as a metamorphosed volcanic conglomerate (A. SCACCHI. La regione vulcanica fluorifera della Campania. Atti Acc. Sc. fis. e. Mat. (2) II. Napoli 1838, No. 2 p. 103).

<sup>4)</sup> Considerazioni sulla genesi del Piperno. Atti Accad. Sc. fis. e Mat. (2) V. Napoli 1893, N<sup>o</sup>. 3. [1891] p. 1—22, reprinted in Giornale di Mineralog'ia, Cristallografia e Petrografia III. Milano 1892, p. 23—54.

<sup>5)</sup> Il piperno. Boll. Soc. Naturalisti. Napoli 1901, p. 34—52 (Geol. Centralbl. VII. Berlin 1905—6, p. 98).

H. J. JOHNSTON-LAVIS, who very emphatically contended for the tufa-character of the piperno, and who attempted to give a peculiar strength to his argument by writing:

“All geologists who have attempted to explain these *principal* “peculiar characters, have utterly failed to do so, and had I space “to enumerate many minor ones, the difficulty would be still greater. “Unfortunately, most of these inclusions have been jumped at, as “the result of that useful instrument though unfortunate misleader “of geology, the microscope, which has caused investigators to forget “that it is only one means to an end, and that field investigation is “of far greater importance.”<sup>1)</sup>

On account of the aversion which JOHNSTON-LAVIS has to the microscope it will be impossible to convince him of the difference between a piperno and a pipernoid tufa. But we point out the fact, that it was exactly the “field-geologists” who, as yet, not knowing anything of the application of “that useful instrument” to the domain of petrography, have ascertained that piperno was an eruptive rock. Besides LEOP. VON BUCH we need only mention SCIPIO BREISLAK<sup>2)</sup>, H. ABICH<sup>3)</sup>, J. ROTH, G. GUISCARDI<sup>4)</sup>. It is likewise a fact known long since that a tufa may obtain a pipernoid structure in the way surmised by JOHNSTON-LAVIS, but the investigators knew, also without the help of the microscope, how to distinguish such like rocks from real piperno.<sup>5)</sup>

The rhyolite of the Pelapis Islands is a stronger evidence of the fact that the piperno-structure is not connected with a tufa-formation as the porosity of the main mass of the rock is as insignificant as that of the “Schlieren” whose form has as little resemblance to that of volcanic ejections.

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1) Notes on the Pipernoid Structure of Igneous Rocks-Natural Science III. London-New-York 1893, p. 219.

2) Voyages physiques et lithologiques dans la Campanie. II. Paris An. IX (1801) p. 42—47.— Institutions géologiques. III. Milan 1818, p p. 154—156.

3) Ueber die Natur und den Zusammenhang der vulkanischen Bildungen. Braunsch. 1841, p. 39.

4) Il piperno. Rendic. Accad. Sc. fis. e Mat. VI. Napoli 1867, p. 221—226.

5) J. ROTH, Der Vesuv und die Umgebung von Neapel. Berlin 1857, p. 512. — G. VOM RATH. Mineralogisch-geognostische Fragmente aus Italien. Zeitschr. d. Deutschen geolog. Gesellsch. XVIII, 1866, p. 633—634.

**Mathematics.** “*Continuous one-one transformations of surfaces in themselves*”. (5<sup>th</sup> communication<sup>1)</sup>). By Prof. L. E. J. BROUWER.

In CRELLE'S Journal, vol. 127, p. 186 Prof. P. BOHL has enunciated without proof the following theorem proved by me (as a particular case of a more general theorem) in vol. 71 of the *Mathematische Annalen* (compare there page 114):

“*Werden die Punkte einer Kugeloberfläche wieder in Punkte der Kugeloberfläche übergeführt und geschieht diese Ueberführung durch stetige Bewegung, welche den Mittelpunkt nicht berührt, so kehrt mindestens ein Punkt in seine frühere Lage zurück. Unter einer stetigen Bewegung ist hier eine Bewegung verstanden, bei welcher die rechtwinkligen Koordinaten stetige Funktionen der Zeit und der Anfangswerte sind.*”

Now I shall show here in the first place that the theorem enunciated and proved in the first communication on this subject<sup>2)</sup>, i. e. that each continuous one-one transformation with invariant indicatrix of a sphere in itself possesses at least one invariant point, may be considered as a particular case of the quoted theorem of BOHL<sup>3)</sup>. To that end I shall establish the following theorem:

“*Any continuous one-one transformation  $\alpha$  with invariant indicatrix of a sphere in itself can be transformed by a continuous modification<sup>4)</sup> into identity<sup>5)</sup>.*”

In order to prove this property we choose in the sphere two opposite points  $P_1$  and  $P_2$  determining a net of circles of longitude and latitude and passing by  $\alpha$  into  $Q_1$  and  $Q_2$ . By means of a continuous series  $\tau$  of conform transformations of the sphere in itself we can transform  $Q_1$  and  $Q_2$  into  $P_1$  and  $P_2$ . Let  $c$  be an arbitrary circle of latitude, described in such a sense that  $P_1$  possesses with respect to  $c$  the order<sup>6)</sup>  $+1$ , and  $c'$  the image of  $c$  for  $\alpha\tau$ , then  $P_1$  possesses also with respect to  $c'$  the order  $+1$ .

1) Compare these Proceedings XI, p. 788; XII, p. 286; XIII, p. 767; XIV, p. 300 (1909—1911).

2) These Proceedings XI (1909), p. 797.

3) This I indicated already shortly *Mathem. Ann.* 71 (1911), p. 325, footnote \*).

4) Under a continuous modification of a univalent continuous transformation we understand in the following always the construction of a continuous series of univalent continuous transformations, i. e. a series of transformations depending in such a manner on a parameter, that the position of an arbitrary point is a continuous function of its initial position and the parameter.

5) That this theorem wants a proof is shown by the fact that e.g. for a torus it does not hold.

6) Compare e. g. J. TANNERY, “*Introduction à la théorie des fonctions d'une variable*”, vol. II, p. 438.



Let  $P$  be an arbitrary point coinciding neither with  $P_1$  nor with  $P_2$  and passing by  $\alpha\tau$  into  $R$ , and let  $Q$  be the point corresponding in latitude with  $P$  and in longitude with  $R$ . Then by transforming the different points  $R$  continuously and uniformly along circles of longitude into the corresponding points  $Q$  we define a continuous series  $\varrho$  of univalent continuous transformations of the sphere in itself with the property that of none of the points  $R$  the path passes through  $P_1$  or  $P_2$ . So an arbitrary curve  $c'$  is transformed by  $\varrho$  into a curve  $c''$ , with respect to which  $P_1$  possesses likewise the order  $+1$ , so that  $c''$  covers the corresponding circle of latitude  $c$  with the *degree*<sup>1)</sup>  $+1$ .

From this ensues that an arc of a circle of latitude connecting an arbitrary point  $P$  with the corresponding point  $Q$  defines unequivocally for any point  $P$  an arc of circle of latitude  $PQ$  whose variation with  $P$  is uniformly continuous, so that it is possible to construct a continuous series  $\varrho'$  of univalent continuous transformations of the sphere in itself, transforming each point  $Q$  into the corresponding point  $P$ , and thereby the transformation  $\alpha\tau\varrho$  into identity. But then  $\tau\varrho\varrho'$  is the looked out for continuous series of transformations, transforming  $\alpha$  into identity.

We shall say that two transformations *belong to the same class*, if they can be transformed continuously into each other. We then can state the theorem proved just now in the following form:

**THEOREM 1.** *All continuous one-one transformations with invariant indicatrix of a sphere in itself belong to the same class.*

As the continuous one-one transformations with invariant indicatrix form a special case of the univalent continuous transformations of degree  $+1$ <sup>2)</sup>, the question arises whether perhaps theorem 1 is a special case of the more general property that all the univalent continuous transformations of the same degree of a sphere in itself belong to the same class. We shall see that this is indeed the case; we shall namely show that any univalent continuous representation of degree zero of a sphere  $\mu$  on a sphere  $\mu'$  can be transformed by continuous modification into a representation of  $\mu$  in a single point of  $\mu'$ , and that any univalent continuous representation of degree  $n \geq 0$  of a sphere  $\mu$  on a sphere  $\mu'$  can be transformed by continuous modification into a *canonical representation of degree  $n$* , i. e. into a representation for which  $n-1$  non intersecting simple closed curves of  $\mu$  are each represented in a single point of  $\mu'$ , whilst the  $n$

1) Mathem. Ann. 71 (1911), p. 106.

2) Mathem. Ann. 71 (1911), p. 106 and 324.

domains determined by these curves are each submitted to a continuous *one-one* representation on  $\mu'$ , and that either all with degree  $+1$  or all with degree  $-1$ . By means of an indefinitely small modification a canonical representation can be transformed into a simply ramified *Riemann representation*, i.e. into a representation which in the sense of analysis situs is identical to a simply ramified representation of a Riemann surface with  $n$  sheets and of genus zero on the complex plane. That all simply ramified Riemann representations belong to the same class, follows, according to a remark made by KLEIN<sup>1)</sup>, out of a known theorem of LÜROTH—CLEBSCH.

In order to transform an arbitrarily given univalent continuous representation  $\alpha$  of  $\mu$  on  $\mu'$  into a representation in a single point, resp. into a canonical representation, we first modify it continuously into a *simplicial approximation*<sup>2)</sup>  $\alpha'$ , to which we have imparted, by means of eventual subdivisions of the corresponding simplicial divisions of  $\mu$  and  $\mu'$ , the property that any base triangle of  $\mu$  covers in  $\mu'$  either a single base triangle, or a single base side, or a single base point; we then investigate the possibility of finding two base triangles of  $\mu$ , one positively and the other negatively represented, allowing that we pass from the one to the other by transversing exclusively base sides of  $\mu$  *not* represented in a single point. If this be the case,  $\mu$  will possess a positively represented base triangle  $t_1$  and a negatively represented one  $t_n$  both represented in the *same* fundamental triangle  $t'$  of  $\mu'$ , allowing us to pass from the one to the other by transversing exclusively such base sides of  $\mu$ , as are represented in the *same* side  $s_1$  of  $t'$ . The base triangles  $t_2, t_3, \dots, t_{n-1}$  of  $\mu$  crossed on this way leading from  $t_1$  to  $t_n$  are then also represented entirely in  $s_1$ .

Let  $s_2$  and  $s_3$  be the other two sides of  $t'$ ; by a continuous modification of  $\alpha'$  and a suitable farther subdivision of  $t_1, t_2, \dots, t_{n-1}, t_n$ , we can generate a representation  $\alpha''$  for which all the triangles  $t_1, t_2, \dots, t_{n-1}, t_n$  are represented entirely in  $s_2$  and  $s_3$ , and which possesses still the same property as  $\alpha'$ , viz. that any base triangle of  $\mu$  covers in  $\mu'$  either a single base triangle, or a single base side, or a single base point.

In the same manner as we transformed  $\alpha'$  into  $\alpha''$ , we transform  $\alpha''$  if possible into  $\alpha'''$ , and we continue this process until after a

<sup>1)</sup> Compare: "*Ueber Riemann's Theorie der algebraischen Funktionen und ihrer Integrale*". Leipzig, 1882.

<sup>2)</sup> Mathem. Ann. 71 (1911), p. 102.

finite number of steps we have reached a representation  $\alpha^{(\nu)}$  no more allowing a suchlike modification.

We now construct on  $\mu$  all those polygons formed by base sides belonging to  $\alpha^{(\nu)}$  which are represented by  $\alpha^{(\nu)}$  in a single point. These polygons divide  $\mu$  into a finite number of domains  $g_1, g_2, \dots, g_k$ . Each domain  $g_\nu$ , which by  $\alpha^{(\nu)}$  is not represented nowhere dense, admits the property that there is no polygon lying entirely within it or partly within it and partly on its boundary, which is represented by  $\alpha^{(\nu)}$  in a single point<sup>1)</sup>. Any two base triangles belonging to the same domain  $g_\nu$  can be connected within  $g_\nu$  by a path transversing only base sides *not* represented in a single point, so that of the base triangles of  $g_\nu$  either no one is represented negatively or no one positively.

As each coherent part of the boundary of  $g_\nu$  is represented on  $\mu'$  by a single point,  $\mu'$  is covered by the image of  $g_\nu$  with a certain *degree* which we will suppose to be positive. Then there are no negative image triangles, but there are in general singular image triangles with two coinciding vertices.

By considering each coherent part  $\gamma_{\nu\tau}$  of the boundary of  $g_\nu$  as a single point  $P_{\nu\tau}$ ,  $g_\nu$  is transformed into a sphere  $sp_\nu$ , and we can deduce a simplicial division of  $sp_\nu$  from the simplicial division of  $g_\nu$  belonging to  $\alpha^{(\nu)}$ , by bisecting all those base sides of  $g_\nu$  which touch the boundary but do not lie in the boundary, dividing by means of these bisecting points each base triangle one side of which lies in the boundary, into a triangle and a trapezium to be considered as a base triangle of  $sp_\nu$ , and dividing those of the remaining base triangles of which sides have been bisected, into new base triangles corresponding to those bisecting points. The simplicial representation  $\alpha^{(\nu)}$  of  $g_\nu$  on  $\mu'$  is then at the same time a simplicial representation of  $sp_\nu$  on  $\mu'$ , whilst by suitable subdivisions of the simplicial divisions

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1) For, as this property holds for polygons formed by base sides, any base triangle of  $g_\nu$  possesses at most one base side represented in a single point. Therefore each broken line, lying in a single base triangle and not in a single base side, which is represented in a single point, must necessarily lie entirely in a straight line segment connecting two points of the circumference not coinciding with vertices. So a polygon represented in a single point must either consist exclusively of base sides, or it can transverse only such base sides as are represented in one and the same base side of  $\mu'$ . In the latter case however the series of the base triangles of  $\mu$  crossed in this way would have to be represented in that selfsame base side of  $\mu'$ , so that each of the two limiting polygons of this series (of which at most one can be illusory) would be a polygon formed by base sides and represented in a single point of  $\mu'$ .

of  $sp_s$  and  $\mu'$  we can effectuate that any base triangle of  $sp_s$  covers in  $\mu'$  either a single base triangle, or a single base side.

By choosing one of the base sides of  $sp_s$  represented by  $\alpha^{(p)}$  in a single point, and considering it as a single point and accordingly the two base triangles adjacent to it as line segments,  $sp_s$  passes into an other sphere  $sp_{s'}$  represented likewise simplicially by  $\alpha^{(p)}$ . In the same way we deduce from  $sp_{s'}$  an other sphere  $sp_{s''}$  if this be possible, and we continue this process until after a finite number of steps we obtain a sphere  $sp_{s^{(r)}}$  no more possessing for  $\alpha^{(p)}$  any singular image triangle.

Let us denote by  $B$  and  $D$  the two base points of  $sp_{s^{(m-1)}}$  identified for  $sp_{s^{(m)}}$  and by  $a$  and  $c$  the two base triangles of  $sp_{s^{(m-1)}}$  contracted into line segments for  $sp_{s^{(m)}}$ . Then the triangles  $a$  and  $c$  have either only the side  $BD$  in common, or moreover a second side, which we may assume to contain the vertex  $B$ .

In the first case we represent the third vertex of  $a$ , resp.  $c$ , by  $A$ , resp.  $C$ , and the domain covered by  $a$  and  $c$  together, by  $d$ . At least one of the base points  $B$  and  $D$ , say  $D$ , does not coincide with a point  $P_{\tau}$ . We then connect in  $sp_{s^{(m-1)}}$  outside  $d$  the points  $A$  and  $C$  by an arc of simple curve  $\beta$  situated in the vicinity of the broken line  $ADC$ , and we represent the domain included between  $\beta$  and the broken line  $ADC$ , by  $d'$ . By means of a continuous series of continuous one-one transformations leaving the points of  $\beta$  invariant and transforming each point of  $AB$  and  $BC$  into points coinciding with it on  $sp_{s^{(m)}}$ , we can reduce the domain  $d + d'$  with its boundary continuously into the domain  $d'$  with its boundary. If we represent by  $\alpha_s^{(m)}$  an arbitrary univalent continuous representation of  $sp_{s^{(m)}}$  on  $\mu'$ , then to the continuous reduction of  $d + d'$  to  $d'$  corresponds a continuous series of univalent continuous representations of  $sp_{s^{(m-1)}}$  on  $sp_{s^{(m)}}$  transforming the representation obtained by the identification of  $B$  and  $D$ , into a continuous one-one correspondence  ${}_m\alpha_{m-1}$  in which the points  $P_{\tau}$  correspond to themselves, thus also a continuous series of univalent continuous representations of  $sp_{s^{(m-1)}}$  on  $\mu'$ , leaving invariant the images of the points  $P_{\tau}$ , and transforming  $\alpha_s^{(m)}$  considered as a representation of  $sp_{s^{(m-1)}}$  on  $\mu'$ , into that representation  $\alpha_s^{(m-1)}$  of  $sp_{s^{(m-1)}}$  on  $\mu'$ , which follows from  $\alpha_s^{(m)}$  by means of  ${}_m\alpha_{m-1}$ .

In the second case we represent the third vertex of  $a$  and  $c$  by  $F$ , choose on the side  $DF'$  of  $a$ , the side  $DF$  of  $c$ , and the common side  $BF'$  successively three such points  $A$ ,  $C$ , and  $G$ , as in passing from  $sp_{s^{(m-1)}}$  to  $sp_{s^{(m)}}$  are brought to coincidence, connect  $A$  within  $a$  rectilinearly with  $B$  and  $G$ ,  $C$  within  $c$  rectilinearly with  $B$  and  $G$ ,

and apply the operation of the first case to the pairs of fundamental triangles  $ABD$  and  $CBD$ ;  $BCG$  and  $FCG$ ;  $BAG$  and  $FAG$  successively <sup>1)</sup>).

By applying this operation successively to  $sp_{\nu}^{(r)}$ ,  $sp_{\nu}^{(r-1)}$ , ...,  $sp''_{\nu}$  and  $sp'_{\nu}$  we experience that the representation  $\alpha^{(\nu)}$  of  $sp_{\nu}$  on  $\mu'$  can be transformed by a continuous modification leaving the images of the points  $P_{\nu\tau}$  invariant, into a representation  $\alpha_h$  of  $sp_{\nu}$  on  $\mu'$ , which follows from  $\alpha^{(\nu)}$  by means of a continuous one-one correspondence between  $sp_{\nu}^{(r)}$  and  $sp_{\nu}$ . As  $sp_{\nu}^{(r)}$  can be divided into elements each of which is submitted for  $\alpha^{(\nu)}$  to a one-one representation of degree  $+1$  on a base triangle of  $\mu'$ , it is clear that  $sp_{\nu}$  can be divided into elements each of which is submitted for  $\alpha_h$  to a one-one representation of degree  $+1$  on a base triangle of  $\mu'$ . The representation  $\alpha_h$  of  $sp_{\nu}$  on  $\mu'$  is therefore a *Riemann representation*, and eventually it may be transformed by an indefinitely small modification leaving the images of the points  $P_{\nu\tau}$  invariant, into a simply ramified Riemann representation.

By executing this process of modification for all the values of  $\nu$  for which it is applicable we arrive at a representation  $\alpha_e$  being for any of the spheres  $sp_1, sp_2, \dots, sp_k$  either a simply ramified, positive or negative Riemann representation, or a representation nowhere dense.

In each domain  $g_{\nu}$  we approximate the boundary parts  $\gamma_{\nu\tau}$  by simple closed curves  $\alpha_{\nu\tau}$  not intersecting each other. Each  $\alpha_{\nu\tau}$  includes with the corresponding  $\gamma_{\nu\tau}$  a domain  $g'_{\nu\tau}$ , and the  $\alpha_{\nu\tau}$  situated in the same domain  $g_{\nu}$  include together a domain  $g'_{\nu}$ . The domains  $g'_{\nu\tau}$  belonging to the same  $\tau$  form together a domain  $g''_{\tau}$ . By means of a continuous series of univalent continuous representations of  $g_{\nu}$  on  $sp_{\nu}$  we can transform identity into a representation which for  $g'_{\nu}$  with the exclusion of its boundaries is a continuous one-one representation on  $sp_{\nu}$ , whilst  $\alpha_{\nu\tau}$  and  $g'_{\nu\tau}$  are represented in  $P_{\nu\tau}$ . By doing this for all values of  $\nu$  we transform  $\alpha_e$  into a representation  $\alpha_l$  being for each of the domains  $g'_{\nu}$  and  $g''_{\tau}$  after contraction of its rims into points either a simply ramified, positive or negative Riemann representation, or a representation nowhere dense.

The domains  $g'_{\nu}$  and  $g''_{\tau}$ , which will be represented henceforth by  $\mathfrak{g}_1, \mathfrak{g}_2, \dots, \mathfrak{g}_u$ , are determined on  $\mu$  by a finite number of simple closed curves not intersecting each other.

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<sup>1)</sup> If we dropped the condition of the invariancy of the images of the points  $P_{\nu\tau}$  (introduced only for the sake of clearness), this second case might have been treated of course in the same manner as the first.

We choose an arbitrary domain  $g_v$ , and suppose in the first place that  $\alpha_l$  is for the sphere  $\sigma_v$  into which  $g_v$  is transformed by contraction of its rims into points, a simply ramified Riemann representation. We then draw on  $\mu'$  a system of ramification sections belonging to this representation and corresponding to a system of simple closed "ramification curves" on  $\sigma_v$ . By first leaving the ramification sections on  $\mu'$  invariant and varying eventually continuously the ramification curves on  $\sigma_v$  in such a manner that after that they contain no more a point corresponding to a rim of  $g_v$ , and then leaving the ramification curves on  $\sigma_v$  invariant and contracting the ramification sections on  $\mu'$  continuously into points, we can transform the representation of  $\sigma_v$  on  $\mu'$  determined by  $\alpha_l$  continuously into a canonical representation. During this continuous modification the points representing the rims of  $g_v$  vary also in general. Let  $i_{\tau}$  be such a rim and  $g_{v\tau}$  the residual domain of  $g_v$  on  $\mu$  determined by  $i_{\tau}$ . We then can follow the continuous variation of the image point of  $i_{\tau}$  by a continuous series of continuous one-one transformations of  $\mu'$  in itself to which corresponds a continuous modification of the representation of  $g_{v\tau}$  on  $\mu'$  determined by  $\alpha_l$ . By applying this modification to the representations of all the residual domains of  $g_v$  we generate a representation  $\alpha'_l$  of  $\mu$  on  $\mu'$  into which  $\alpha_l$  can be transformed continuously, and which is a canonical representation for  $\sigma_v$ .

In the second place we suppose  $\alpha_l$  to be for  $\sigma_v$  a representation nowhere dense. Then we can modify the representation of  $\sigma_v$  on  $\mu'$  determined by  $\alpha_l$  into a representation in a single point. The variation of the image points of the rims of  $g_v$  implied by this modification, can be followed once more in the way described above by a continuous modification of the representation of the residual domains of  $g_v$ , furnishing us with a representation  $\alpha'_l$  of  $\mu$  on  $\mu'$  into which  $\alpha_l$  can be transformed continuously, and which represents  $\sigma_v$  in a single point.

By executing this operation for all values of  $v$  successively, we get a representation  $\alpha_l^{(2)}$  of  $\mu$  on  $\mu'$ , into which  $\alpha_l$  can be transformed continuously, and which represents each of the domains  $g_1, g_2, \dots, g_u$  either after contraction of the rims into points canonically, or in a single point. The sphere  $\mu$  is now divided by a finite number of non intersecting simple closed curves into a finite number of domains  $d_1, d_2, \dots, d_w$  in such a way that for  $\alpha_l^{(2)}$  each of these domains is submitted either after contraction of the rims into points to a continuous one-one representation, or to a representation in a single point. Thus the degree of these representations is 0,  $\neq 1$ , or

— 1, according to which we distinguish domains of the first, the second, and the third kind.

If for the representation  $\alpha_f^{(\psi)}$ , which may be denoted henceforth by  $\alpha_f$ , all domains  $d_\nu$  are of the first kind, we have attained our aim; for then we have transformed  $\alpha$  continuously into a representation of  $\mu$  in a single point of  $\mu'$ . So we further confine ourselves to the case that among the  $d_\nu$  there are domains of the second or of the third kind, and we will suppose that there occur moreover domains of the first kind. Then there is certainly a domain  $d_\gamma$  of the first kind adjacent to a domain  $d_\xi$  of the second or third kind. The domain formed by  $d_\gamma$  and  $d_\xi$  together, may be indicated by  $d_{\gamma\xi}$ , the sphere deduced from  $d_{\gamma\xi}$  by contraction of its rims into points, by  $\sigma_{\gamma\xi}$ . We then can modify the univalent continuous representation of  $\sigma_{\gamma\xi}$  on  $\mu'$  determined by  $\alpha_f$  continuously into a continuous one-one representation of  $\sigma_{\gamma\xi}$  on  $\mu'$ . The variation of the image points of those rims of  $d_{\gamma\xi}$  which originate from  $d_\gamma$  necessarily implied by this modification, can once more be followed in the manner described above by a continuous modification of the representation determined by  $\alpha_f$  of those residual domains of  $d_{\gamma\xi}$  which originate from  $d_\xi$ , furnishing us with a representation  $\alpha'_f$  distinguishing itself thereby from  $\alpha_f$  that a domain of the first kind and a domain of the second (resp. third) kind have been united into a single domain of the second (resp. third) kind.

By repeating this operation as many times as possible we arrive after a finite number of steps at a representation  $\alpha_f^{(\tau)}$ , distinguishing itself thereby from  $\alpha_f$  that all the domains of the first kind have been absorbed by domains of the second and of the third kind.

If there are for the representation  $\alpha_f^{(\tau)}$ , which may be denoted henceforth by  $\alpha_q$  domains of the second as well as of the third kind, we consider a domain  $d_\pi$  of the second kind separated by a simple closed curve  $i_{\pi\rho}$  from a domain  $d_\rho$  of the third kind, and we represent the domain formed by  $d_\pi$  and  $d_\rho$  together, by  $d_{\pi\rho}$ , and the sphere deduced from  $d_{\pi\rho}$  by contraction of its rims into points, by  $\sigma_{\pi\rho}$ . Moreover we represent by  $P_1$  the image point of  $i_{\pi\rho}$  for  $\alpha_q$ , by  $P_2$  the opposite point of  $P_1$  on  $\mu'$ , and we modify the representation of  $\sigma_{\pi\rho}$  determined by  $\alpha_q$  into a representation of  $\sigma_{\pi\rho}$  in the single point  $P_2$ , by diminishing the polar distances measured from  $P_2$  continuously and proportionally to each other to zero. The variation of the image points of the rims of  $d_{\pi\rho}$  necessarily implied by this

modification, can be followed in the manner described above by a continuous modification of the representation of the residual domains of  $d_{\pi\epsilon}$  determined by  $\alpha_q$ , furnishing us with a representation  $\alpha_q'$  distinguishing itself thereby from  $\alpha_q$  that a domain of the second and one of the third kind have been united into a single domain of the first kind; this domain however, if it does not occupy the whole sphere  $\mu$ , can be absorbed in the manner described above by an adjacent domain of the second or of the third kind, by which process  $\alpha_q'$  passes continuously into a representation  $\alpha_q''$ , distinguishing itself thereby from  $\alpha_q$  that a domain of the second and one of the third kind have been absorbed together by a domain of the second resp. of the third kind.

By repeating this operation as many times as possible we arrive after a finite number of steps at a representation  $\alpha_q^{(n)}$  for which the domains  $d_i$  are either all of the second or all of the third kind. So this representation is a *canonical* one, and we have proved:

**THEOREM 2.** *All univalent continuous transformations of the same degree of a sphere in itself belong to the same class.*

A proof of the inverse theorem has been given *Mathem. Ann.* 71, p. 105.

In carrying out the ideas sketched in the second communication on this subject<sup>1)</sup> I experienced that in some points of the course of demonstration indicated there, still a tacit part is played by the Schoenfliesian theory of domain boundaries criticized by me<sup>2)</sup>, so that the theorems 1 and 2 formulated p. 295 and likewise the "general translation theorem" founded upon them and enunciated without proof *Mathem. Ann.* 69, p. 178 and 179, cannot be considered as proved<sup>3)</sup>, and a question of the highest importance is still to be decided here.

The "plane translation theorem" stated at the end of the second communication (p. 297) and likewise *Mathem. Ann.* 69, p. 179 and 180, has meanwhile been proved rigorously by an other method.<sup>4)</sup>

<sup>1)</sup> These Proceedings XII (1909), p. 286—297.

<sup>2)</sup> Compare *Mathem. Ann.* 68 (1910), p. 422—434.

<sup>3)</sup> Already the property of p 288 that the transformation domain constructed in the way indicated there determines at most two residual domains, vanishes for some domains incompatible with the Schoenfliesian theory.

<sup>4)</sup> Compare *Mathem. Ann.* 72 (1912), p. 37—54.



**Chemistry.** — “*Extension of the theory of allotropy. Monotropy and enantiotropy for liquids.*” By Prof. A. SMITS. (Communicated by Prof. A. F. HOLLEMAN).

The extension meant above concerns the case that the pseudo-binary system exhibits the phenomenon of unmixing in the liquid state.

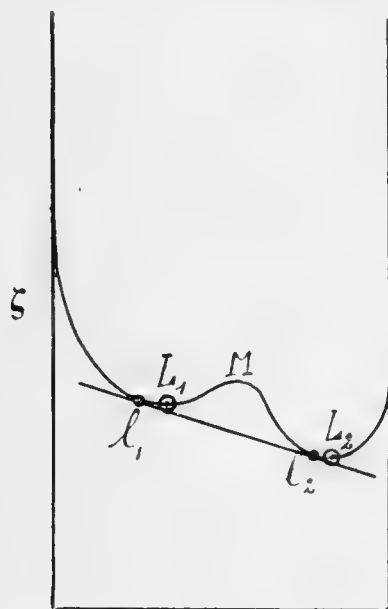


Fig. 1 X.

Let the  $\zeta, x$ -line be schematically represented by fig. 1 at the temperature and pressure at which the phenomenon of unmixing takes place. Then in the first place it is noteworthy that  $l_1$  and  $l_2$  are the coexisting liquid phases of the pseudo-binary system, and that moreover there exist two minimum points  $L_1$  and  $L_2$  representing the liquid phases which may be formed when the system gets in internal equilibrium, and consequently behaves as a unary substance.

The two liquid phases are not miscible, and when they are brought into contact the metastable liquid  $L_1$  will pass into the stable liquid phase  $L_2$ , so that this operation means the same thing as seeding the metastable liquid. As fig. 1 shows the *metastable* unary liquid point  $L_1$  lies inside, and the *stable* unary liquid point  $L_2$  outside the region of incomplete miscibility, and now it is of importance to examine what happens when we move toward such a temperature that the critical phenomenon of mixing occurs in the pseudo-binary system. The coexisting phases  $l_1$  and  $l_2$  have drawn nearer and nearer to each other, and finally coincided in the critical mixing-point, and the  $\zeta, x$ -line has then changed into a curve with only one minimum, as fig. 2 shows.

It is now, however, of importance for our purpose to consider the way in which the  $\zeta, x$ -line has changed its form from that of fig. 1 to that of fig. 2.

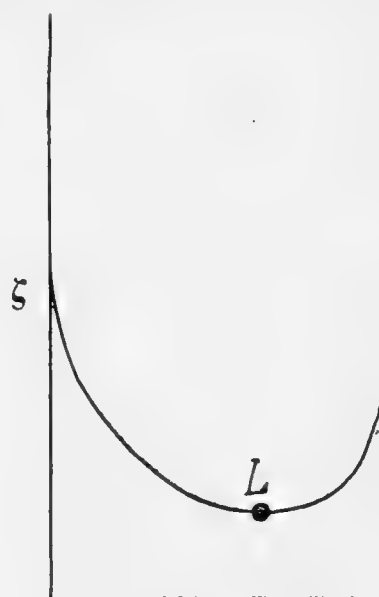


Fig. 2 X.

It is known that before the points  $l_1$  and  $l_2$  coincide, the maximum

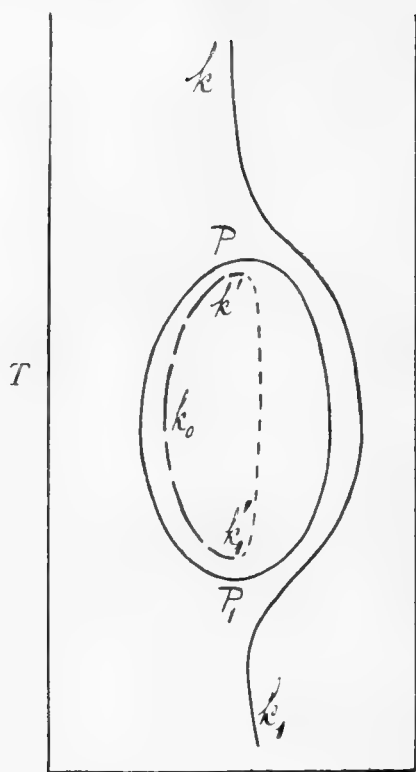


Fig. 3 x.

$M$  vanishes in consequence of the coincidence of this point with the minimum  $L_1$ , at which moment a point of inflection appears with horizontal tangent. At this moment the possibility of the existence of a metastable unary liquid ceases, so that this condition has already become impossible before the critical mixing point has been reached in the pseudo-system. This consideration is in itself already sufficient to indicate in a  $Tx$ -diagram the situation of the liquid lines in the unary system with respect to those in the pseudo-binary one. If we assume that the pseudo-system, just as the system *nicotine-water*, presents an upper and a lower critical mixing point, fig. 3. is formed.

The closed line  $PP_1$  indicates the coexisting liquid phases in the pseudo-binary system. Outside the region enclosed within this continuous curve, runs the line  $kk_1$ , on which the stable internal liquid equilibria are found, and inside this region lie the metastable internal liquid equilibria on the line  $k'_1 k_0 k'^1$ ). In the points  $k'_1$  and  $k'$  this line passes continuously into the locus of the maximum points  $M$  of the  $\xi$ - $x$ -lines, and as in these points  $\left(\frac{\partial \xi}{\partial x}\right)_{P,T} = 0$ , just as for the stable and metastable unary equilibria, but  $\left(\frac{\partial^2 \xi}{\partial x^2}\right)_{P,T} < 0$ , we may call the locus of the maximum points  $M$  the line of the *unstable* internal equilibria.

The theory of *allotropy* attributes the phenomena of monotropy and enantiotropy to the occurrence of different kinds of molecules of one substance, and says that when there exist two or more solid states of a substance, the differences in properties are owing to the situation of the internal equilibrium which will be different in the two solid states.

Now we saw just now that when a substance occurs in two different liquid states, this phenomenon must also be ascribed by the theory to the existence of two different internal equilibria between different kinds of molecules of the same substance. So according to

1) The lines of the internal equilibria have here a very peculiar shape, which is dependent on the phenomenon of unmixing. I shall return to this subject later on.

this new view there is no essential difference between the occurrence of different solid and different liquid phases of one substance and as in the case considered here we have two liquid phases, one of which is *always* stable with respect to the other, we are justified in speaking here of the phenomenon of *monotropy for a liquid*.

Now it is of importance to examine what will take place when the region of incomplete miscibility comes into contact with one of the melting-point lines of the pseudo-binary system.

Beforehand I will, however, remark that Dr. SCHOEVERS<sup>1)</sup>, who undertook the same problem at BAKHUIS ROOZEBOOM's instigation, but took no notice of the  $\xi$ - $x$ -lines, could only draw by chance a line for the stable unary liquid equilibrium, as shown in fig. 4.

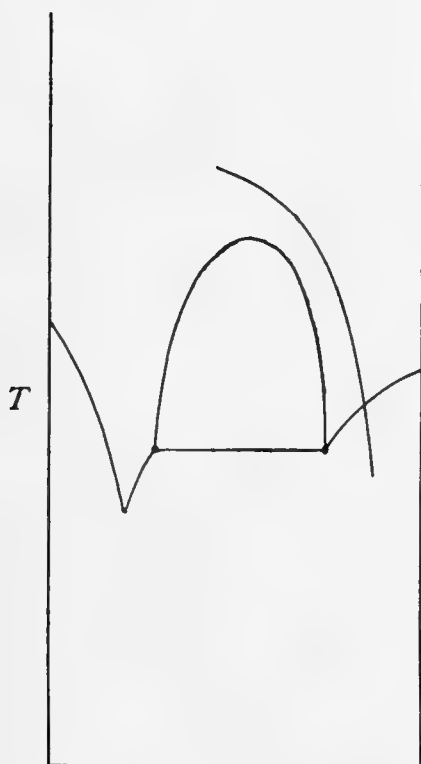


Fig. 4 X.

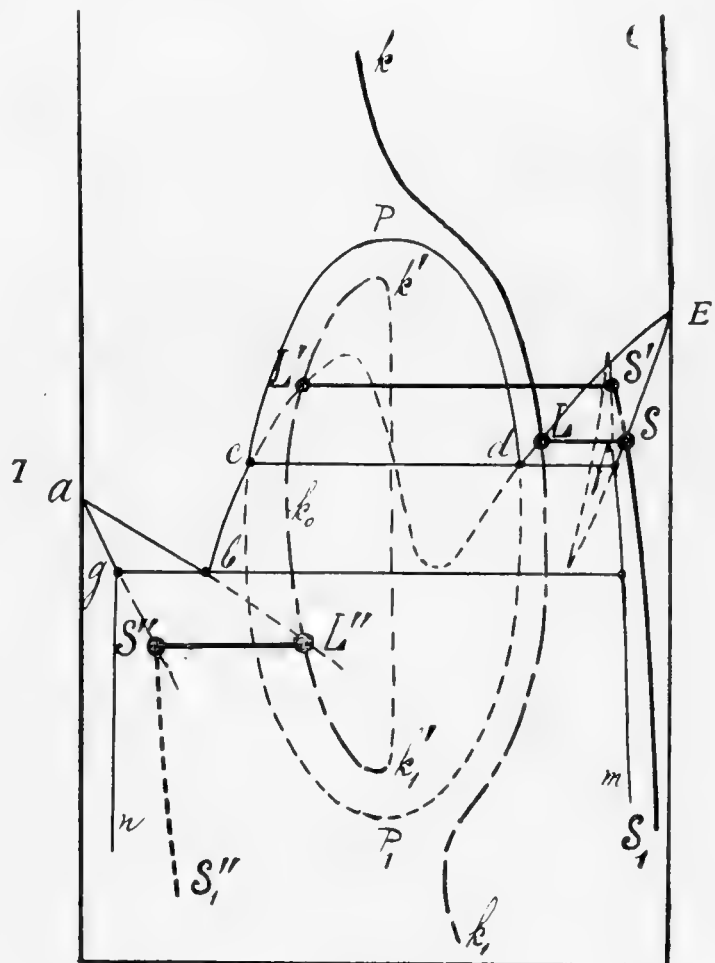


Fig 5 X.

If we suppose that the region of incomplete miscibility comes in contact with the melting-point line of the component with the higher melting-point, we get the  $T, x$ -figure 5.

Now it is of importance to determine the continuity between the two pieces  $ed$  and  $cb$  of the interrupted melting-point line of the pseudo-component  $B$ , and also the continuity which is connected with it, between the mixed crystal lines  $ef$  and  $mf$ . Now it is the question where the liquid lines of the unary system will meet those

<sup>1)</sup> Thesis for the doctorate.

of the pseudo-binary system. In the first place we see that the stable unary liquid line meets the melting-point line of the pseudo-system in  $L$ , so that there a total solidification will take place, at least if phenomena of retardation fail to appear.

The solid states, which are in internal equilibrium below this temperature, and so belong likewise to the unary system, lie on the line  $SS_1$ . It is further noteworthy that one of the two metastable parts of the melting-point line of the pseudo-component  $B$ , intersects the metastable liquid line of the unary system in  $L'$ .

At the temperature of this point of intersection an intersection must also take place of the metastable produced parts of the mixed crystal line  $mf$  and of the line for the solid internal equilibrium  $S_1S$ , which intersection is denoted by the point  $S'$ .

It follows from this that when the metastable unary liquid is cooled down, and no retardation takes place, at  $L'$  total solidification to the metastable unary solid phase  $S'$  will set in, which, however, becomes stable at  $S$ . So what is remarkable about this, is that the metastable point of solidification lies *higher* than the stable one, and this is due to this that here there is no monotropy in the solid state but monotropy in the liquid state, in consequence of which we get the reverse of what we are accustomed to, as is immediately clear, when we draw the  $P, T$ -fig. Our  $T, X$ -fig. 5, however, reveals more. We see namely from it that when the metastable part of the region of incomplete miscibility extends far enough below the eutectic point of the pseudo-system, the metastable unary liquid line can also be cut by the metastable prolongation of the melting-point line of the pseudo-component  $A$ , so that the possibility also exists that in  $L''$  total solidification of the metastable unary liquid to the metastable unary solid substance  $S''$  sets in, which solid phase will then follow the line  $S''S_1''$  at lower temperatures. So one of the peculiarities of this case consists in this that the metastable unary liquid possesses *two* metastable points of solidification, and that when this liquid is not converted to a stable one, it can solidify to a solid substance which is at first metastable and at lower temperatures stable when it is first heated above a definite temperature, and then cooled down. If the temperature is not raised so high, the metastable unary liquid solidifies to another solid substance, which remains metastable, at least when no transition equilibrium occurs in the solid state.

Now it should, however, be pointed out that the two mentioned points of solidification of the metastable unary liquid need not necessarily exist. The upper point of solidification may be absent, in con-

sequence of the partially metastable, partially unstable middle portion of the melting-point line of the pseudo-component *B* no longer intersecting the metastable unary liquid line, but running round this curve. And the lower point of solidification may be absent, when the same curve lies entirely above the metastable prolongation of the melting-point line of the pseudo-component *A*.

When the question is considered in what way in case of liquid monotropy, the metastable phase can be obtained from the stable one, one arrives at the conclusion that this will have to take place by rapid condensation of the vapour, which in concentration is nearer the metastable than the stable liquid.

Whether substances have already been found which belong to the above-described type, is still open to doubt, though in the literature statements are found, which might lead us to suppose so.

As is known, it was believed for a long time that the pseudo-system of sulphur had to possess a region of unmixing, because it was thought that some phenomena observed in the investigation furnished indubitable indications in this direction. This view was first pronounced by BAKHUIS ROOZEBOOM, and supported by KRUYT, on the ground of his own observations <sup>1)</sup>. After SMITH c.s. <sup>2)</sup> had made it probable that the quasi-unmixing was to be ascribed to a difference of temperature, I succeeded last year in conjunction with Dr. DE LEEUW <sup>3)</sup> in ascertaining with perfect certainty that the phenomenon in question has nothing to do with a phenomenon of unmixing, and is really brought about by a difference of temperature, which gives rise to a quasi-unmixing when tubes with more than a certain inner diameter are used.

Moreover it appeared that the point of solidification of states of sulphur fixed at higher temperatures could not give support to the old view, so that not a single reliable experimental datum is now known that speaks in favour of the existence of a region of incomplete miscibility in the pseudo-system.

That the shape of the line for the stable unary liquid equilibrium resembles that of the line *kL* in Fig. 5, is of course, of not the slightest importance, for also when the pseudo system possesses no region of incomplete miscibility in the liquid state, the said line can have such a shape. Besides, the system sulphur, as I already stated, is at least pseudo-ternary, which view is in harmony with the

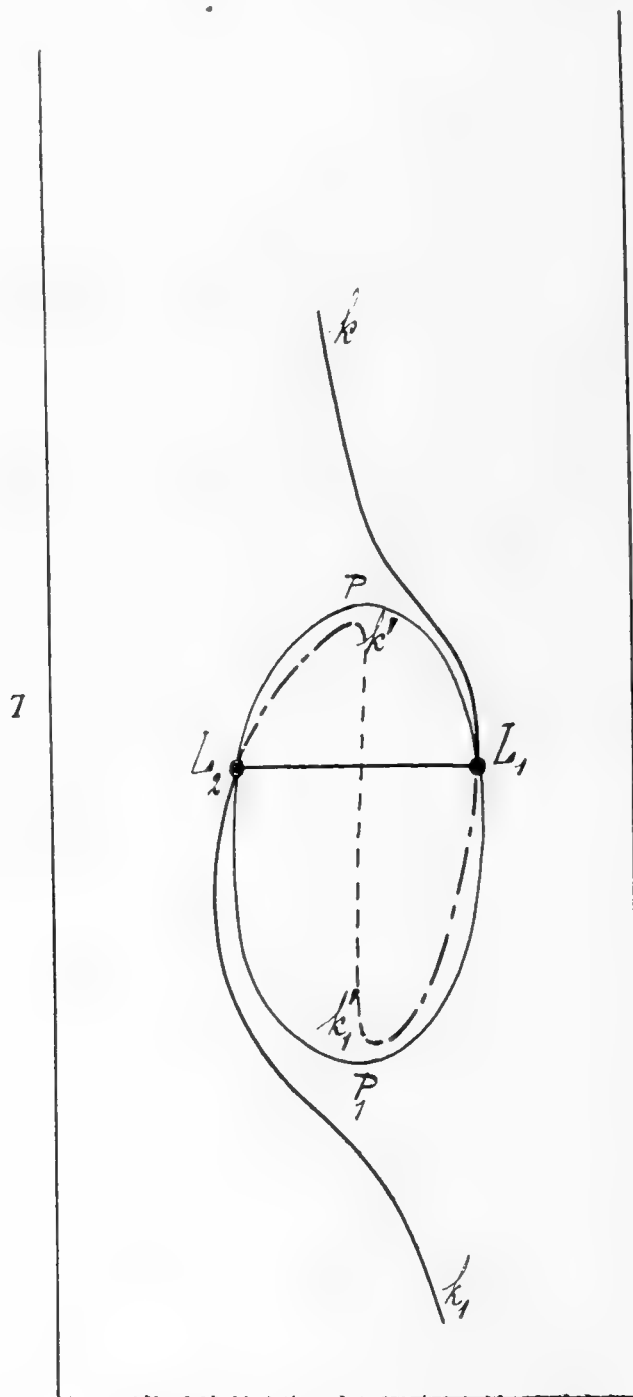
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<sup>1)</sup> Z. f. phys. Chem. **64**, 513 (1908).

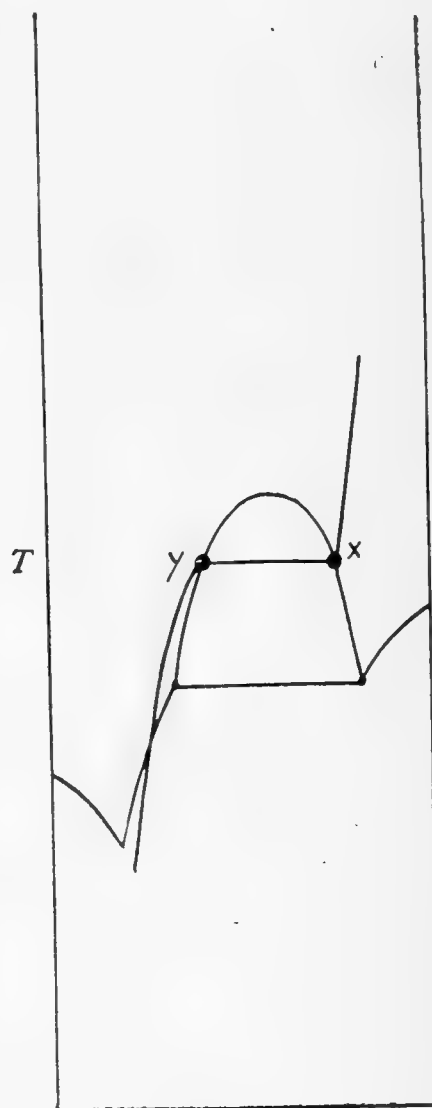
<sup>2)</sup> " " " " **57**, 685 (1907).

<sup>3)</sup> These Proc. Oct. 1911, p. 461.

results of the investigations of ROTENJANZ<sup>1)</sup> and ATEN<sup>2)</sup>. In a more complicated case, in which a line of equilibrium is the resultant of three or more lines of equilibrium a line of equilibrium with a clearly marked point of inflection will of course exceedingly easily arise, as is, indeed, the case for the aldehydes<sup>3)</sup>.



X  
Fig. 6.



X  
Fig. 7.

2. Let us suppose in the second place that above the temperature of the three-phase equilibrium  $S_B + L_1 + L_2$  the  $\zeta$ - $x$ -line of fig. 1

<sup>1)</sup> Z. phys. f. Chem. **62**, 609 (1908).

<sup>2)</sup> See Versl. Kon. Ak. 28 Sept. 1912, p. 396. This paper will shortly appear in These Proceedings

<sup>3)</sup> Z. f. phys. Chem. **77**, 269 (1911).

changes in such a way that the minimum point  $L_2$  gets higher than  $L_1$ , so that a change of stability takes place. Under these circumstances we get what I discussed before for the solid phase. At the moment that the minimum points lie at the same height, the unary liquid phase will suddenly be changed into one of different concentration, if no retardation takes place.

So in this case we have enantiotropy for a liquid or a liquid with a point of transition.

The  $(T, x)_P$ -fig. of the pseudo-binary and unary system can then have the form as indicated in fig. 6, when the equilibria with solid substance are omitted.

We see from this that the two stable unary liquid lines  $kL_1$  and  $L_2k_1$  are continuously connected with each other by a partially metastable, partially unstable middle portion, and that in accordance with the theory of allotropy the equilibrium between the two phases

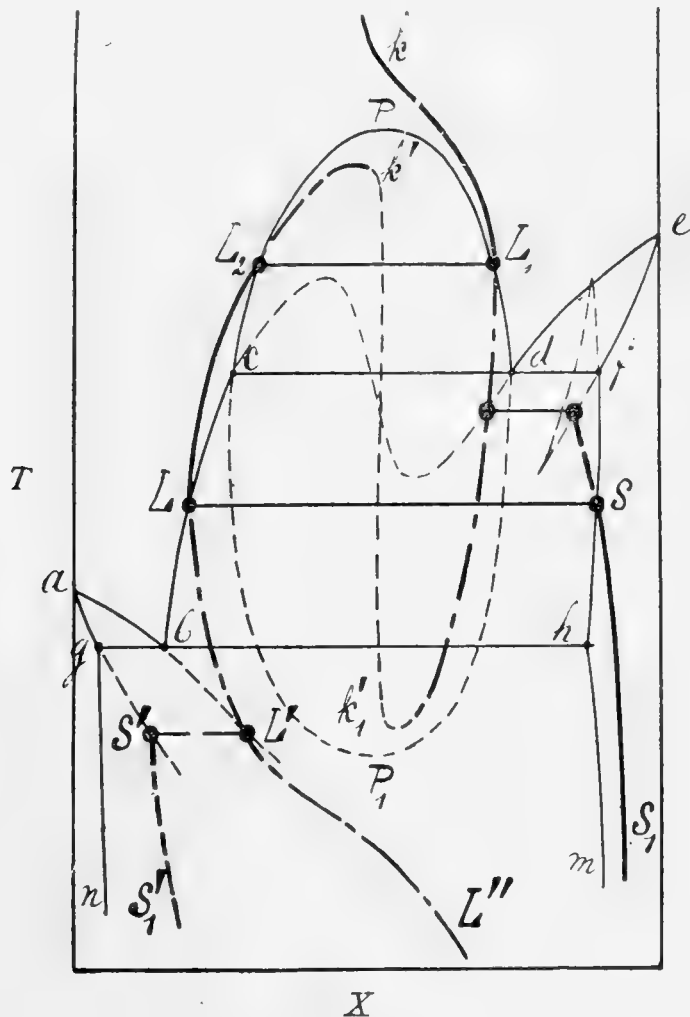


Fig. 8.

$L_1$  and  $L_2$  is perfectly comparable with the equilibrium between two solid phases at the temperature of transition.

If we now examine what may happen when the region of incom-

plete miscibility in the pseudo system comes in contact with one of the melting-point lines, we may distinguish different cases. In his Thesis for the Doctorate SCHOEVEERS gives the following figure 7, adding that when on loss of heat the phase  $x$  has been entirely converted to  $y$ , the ordinary phenomena will occur at lower temperatures.

By ordinary phenomena SCHOEVEERS understands the deposition of one of the two components in pure state. The theory of allotropy, however, says that from the liquid which is in internal equilibrium, a solid substance will deposit, which is also in internal equilibrium, so that this solid phase will contain the two pseudo-components. If we express this in a drawing, we may get among others fig. 8, which is at once clear without any further elucidation. It is, however, necessary to point out that it is also possible that the line for the internal liquid equilibrium  $L_2LL'L''$  does not intersect the stable part of the melting-point line of the pseudo-component  $B$ , but that of the pseudo-component  $A$ . Besides it is possible that coming from higher temperatures the line for the internal liquid equilibrium does not meet the region of incomplete miscibility for the first time on

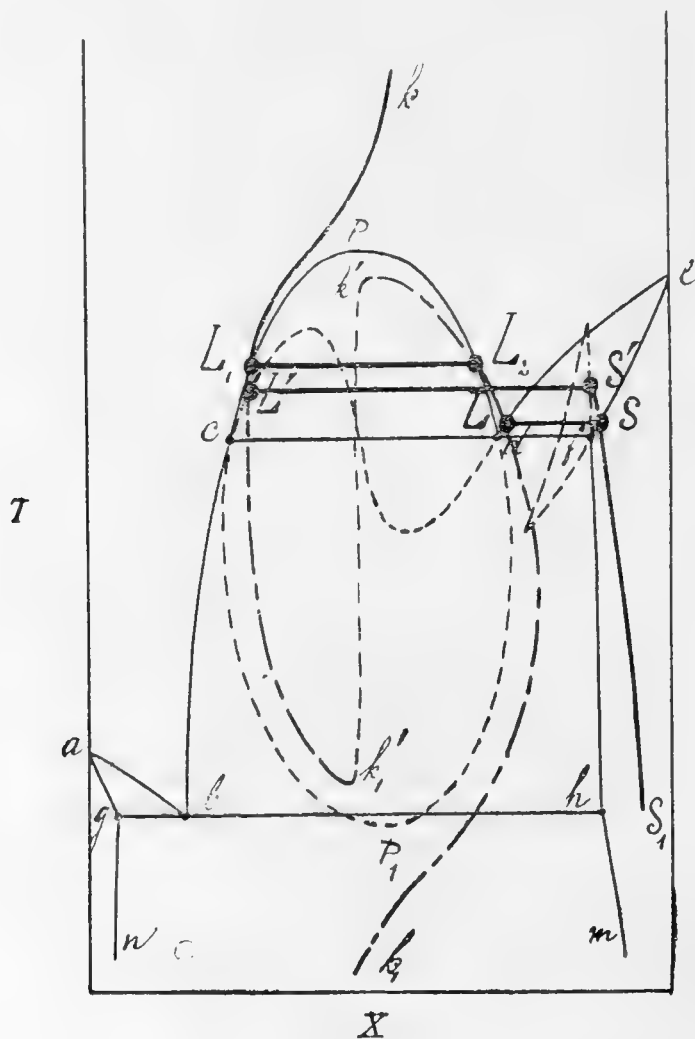


Fig. 9.



the righthand side, but on the lefthand side, in which case fig. 9 gives one of the possible situations. The region of incomplete miscibility lies too high here to give the second lower metastable unary point of solidification.

All these  $T,x$ -figures can be accurately determined by means of the  $\zeta$ - $x$ -lines, which has been omitted here for want of space.

It may finally be remarked that the phenomenon of enantiotropy for liquids has never been observed as yet, but the possibility of this phenomenon is beyond all doubt.

*Anorg. chem. laboratory of the University.*

*Amsterdam, Sept. 20, 1912.*

**Chemistry.** — “*The application of the theory of allotropy to the system sulphur*”. II. By Prof. A. SMITS. (Communicated by Prof. A. F. HOLLEMAN).

In a preceding communication<sup>1)</sup> I already pointed out that the theory of allotropy requires that the system sulphur must be considered to be at least *pseudo-ternary*.

On that occasion a  $T,x$ -figure was projected by me, which as I stated already then, had still to undergo a simplification by the omission of the region of incomplete miscibility<sup>2)</sup>. But the figure had to be modified also in another respect, for in the meantime SMITH and CARSON<sup>3)</sup> had determined the melting-point line of a third crystallised modification of the sulphur, the so-called *soufre nacré* (mother-of-pearl sulphur), which had been discovered by GERNEZ<sup>4)</sup>.

To keep the representation as simple as possible for the present, the modification required to insert this third crystallised condition of sulphur into our figure, has been accomplished by assuming in the pseudo binary system  $S_R—S_M$  and  $S_M—S_\mu$ <sup>5)</sup> above the eutectic point a discontinuity in the monoclinic mixed crystals. In consequence of this the line for the internal liquid equilibrium in the plane for the pseudo-binary system  $S_R—S_M$  meets the stable melting-point line of one kind of monoclinic mixed crystals in  $l_2$ , and the metastable branch of the melting-point line of the other kind of monoclinic mixed crystals in  $l_0$ , the same line of equilibrium cutting the metastable part of the

1) These Proc. XIV 263.

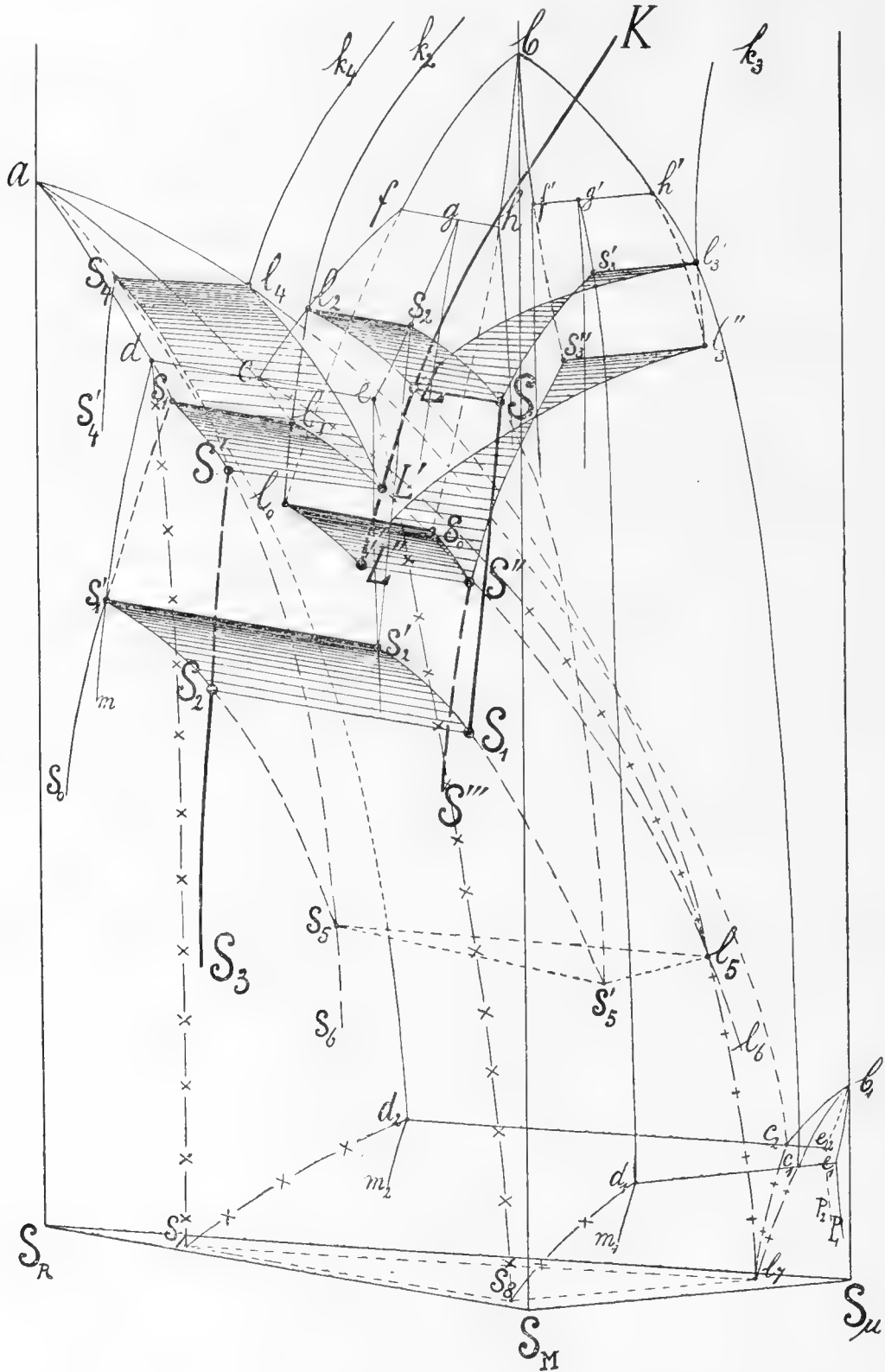
2) „ „ XIV 461.

3) Zeitschr. f. phys. Chem. 77, 661 (1912).

4) Journ. de phys. 3, 76 (1884).

5) By  $S_R$ ,  $S_M$ ,  $S_\mu$  the pseudocomponents are meant here.

melting-point line of the rhombic mixed crystals in  $l_1$ . If we have once premised this in the plane for  $S_R + S_M$ , we find the ternary  $T, x$ -figure in the same way as was explained in my first communication on this subject, if viz. the fact is allowed for that the transi-



tion point is lowered by the third component, which follows from the experiments carried out by Dr. DE LEEUW at my request<sup>1)</sup>.

<sup>1)</sup> See Versl. Kon. Ak. 28 Sept. 1912, p. 488. This paper will shortly appear in These Proceedings.

In this  $T,x$ -figure **L** and **S** denote the coexisting phases at the unary point of solidification of the *monoclinic* sulphur, and in the same way the points **L''** and **S''** indicate the coexisting phases at the unary point of solidification of the monoclinic *soufre nacré*, **L'** and **S'** referring to the unary point of solidification of *rhombic* sulphur, and **S<sub>1</sub>** and **S<sub>2</sub>** to the coexisting solid phases at the unary point of transition.

In conclusion I will *emphatically* point out that it is very well possible that in many respects the real  $T,x$ -figure of the system sulphur deviates from the diagram given here. The system sulphur may be pseudo-quaternary, or even still more complicated. Moreover it is very well possible, indeed it is even probable, that in the pseudo-binary systems no eutectic points occur etc., but, however strange this may seem, this is just now of minor importance.

At present the only end in view can be this to find a means to express the fundamental thought, that we meet here with a system that is composed of more than two kinds of molecules, and of which not only the unary vapour- and liquid phases, but also the unary solid phases are states in which these different kinds of molecules are in equilibrium. Starting from this idea the figure given here was drawn up, which will probably appear to be able for the present to account satisfactorily for the observed phenomena.

Amsterdam, Sept. 25 1912. *Anorg. chem. lab. of the University*

**Chemistry.** — “*The inverse occurrence of solid phases in the system iron-carbon.*” By Prof. A. SMITS. (Communicated by Prof. A. F. HOLLEMAN.)

Through an investigation made by RUFF<sup>1)</sup> concerning the completion of the  $T,x$ -figure of the system iron-carbon I came to the conclusion some time ago that stable carbides probably occur in this system<sup>2)</sup>. Shortly after there appeared an abstract of a preliminary investigation by WITTOFF<sup>3)</sup>, written in Russian, which seemed to confirm this surmise. When what seems very probable to me, the results of WITTOFF are correct, we meet in the system iron-carbon with a peculiarity, as I demonstrated before, which has been met with up to now only in the system cerium sulphate-water. This peculiarity consists in the inverse occurrence of solid phases. One of

<sup>1)</sup> Metallurgie 458, 497 (1911).

<sup>2)</sup> Z. f. Elektr. Chem. 18, 362 (1912).

<sup>3)</sup> Russ. phys. chem. Ges. 43, 1613 (1911). Compt. rend 1912, 1091.

the phases which shows this phenomenon in the system iron-carbon, is *graphite*. Graphite is the second component, and when there was no deviation from the ordinary state of things the succession of the solid phases, which coexist with the saturated *solid* and *liquid* solutions, would be such that the carbon content continually increased in one direction. Starting at the ordinary temperature we find, however, this that first graphite, and then carbides are formed, which latter however will finally have to give way before the graphite again.

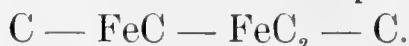
Now it would follow from the preliminary investigations of WITTORF, when namely the equilibria examined by him are stable, that twice such an inverse deposition takes place in the system *iron-carbon*, for with rise of temperature he found this succession:



from which it appears that a solid phase with a *higher* percentage of iron succeeds not only *C*, but also *Fe C*.

This phenomenon of inverse occurrence of solid phases is still so strange to us that it is expedient theoretically to enter a little more deeply into this matter.

To throw the peculiar element into strong relief, I shall discuss the phenomenon led by the same example as I used as an illustration in the Zeitschr. f. Elektrochemie. So I shall suppose for a moment that the succession of the solid phases which coexist with saturated liquid solutions with rise of temperature, is this:



If we now suppose that the situation of the lines for the three-phase equilibrium with one of these solid phase, so for  $S + L + G$ , is as has been represented in fig. 1, the easiest way to find the situation of the other three-phase lines is to prolong the two three-

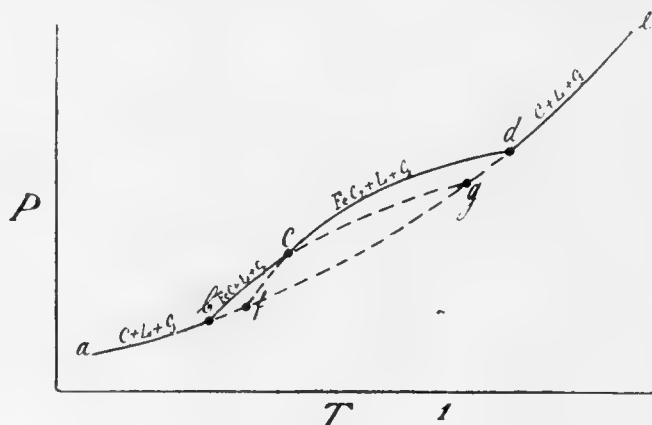


Fig. 1.

phase lines *bc* and *dc* metastable through the point of intersection *c*, till we meet the metastable middle portion of the three-phase line for  $C + L + G$  in *g* resp. *f*.

Let us at first only consider the two three-phase lines for C + L + G and FeC + L + G, which are once more drawn separately in fig. 2. Then it is noteworthy that *b* and *g* are two quadruple points, where vapour, liquid, graphite and the carbide FeC coexist. There is,

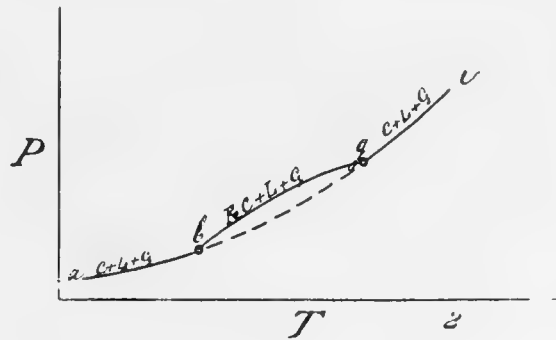


Fig. 2.

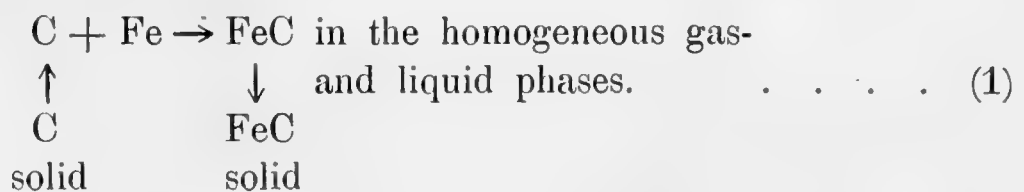
however, a difference between these two quadruple points, and the most essential difference is this that whereas in the first quadruple point *b* with supply of heat graphite with the vapour and the liquid phase is converted to FeC, in the second quadruple point the very reverse takes place.

If the case supposed here actually existed, we might account for it in the following way. The simplest supposition we can make is that along the three-phase line for C + L + G the concentration of FeC in the vapour and in the liquid phase continually increases from *a* to *b*, because the carbon concentration increases, and because besides we probably have here the endothermic process:



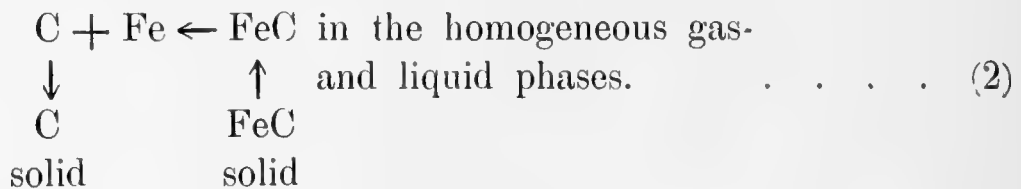
In consequence of the shifting of the above mentioned equilibrium to the right; the liquid and the vapour phases in the quadruple point *b* have just become saturate with FeC, and they are still just saturate with graphite. With an infinitely small rise of the temperature the two phases, which are still supposed to be in contact with graphite, become *supersaturate* with regard to FeC, and *unsaturate* with regard to graphite, from which follows that on supply of heat graphite will dissolve and FeC deposit in the quadruple point *b*, till all the graphite is gone.

So the symbol for the conversion, which takes place in the quadruple point *b* on *supply of heat* is as follows:



It is clear that if the reverse happens in the quadruple point  $g$ , the condition must have become different in so far that the homogeneous gaseous resp. liquid phases,\* which were before saturate with regard to FeC and unsaturate with regard to C, must be saturate again in  $g$  with respect to both the solid phases, and infinitely little above the temperature of the quadruple point  $g$  the gaseous and liquid phases in contact with solid FeC must become unsaturate with respect to FeC, and supersaturate with respect to graphite, so that solid FeC is dissolved, and graphite is deposited, till all the carbide is gone.

So in the quadruple point  $g$  we get for the transformation on supply of heat the symbol



So the transformation given here must be endothermic in the direction of the arrows. We have to call attention to the fact that we assumed for shortness'sake that the formation of FeC in the coexisting gas and liquid phases is endothermic along the three phase line for  $\text{C} + \text{L} + \text{G}$  from  $a$  to  $b$ . Now, however, we know only with certainty that the total transformation (1) is attended with absorption of heat.

When in the process of condensation resp. solidification of FeC from the coexisting phases more heat was developed than was absorbed in the process of evaporation resp. melting of graphite <sup>1)</sup>, the process in the homogeneous phases would undoubtedly be *endothermic*, but in the opposite case the total transformation (1) could be endothermic, whereas the reaction in the homogeneous gas and liquid phases was *exothermic*. But in this case we should have to inquire how it is possible that the gas and liquid phases, which were unsaturate with respect to FeC on the three-phase lines between the points  $a$  and  $b$ , have become saturate with respect to this compound at  $b$ . This is easy to see. We must namely consider two influences here which can displace the equilibrium: in the first place the temperature, and in the second place the concentration of the reacting components. On rise of temperature in the absence of graphite the equilibrium in the homogeneous gas and liquid phases would shift to the left, but in the presence of graphite just the reverse would take place, when namely the increase of solubility of graphite predominates over

<sup>1)</sup> The heat of mixing included.

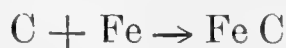
the influence of the temperature on the homogeneous equilibrium on rise of temperature.

Thus we may not conclude from the circumstance that the transformation (2), which refers to the second quadruple point  $g$  is endothermic, that the conversion in the homogeneous phase proceeds endothermically in the direction of the arrow.

If we make the same supposition as we did just now, viz. this that in the process of evaporation resp. melting of FeC more heat is absorbed than is developed by the process of condensation resp. solidification of graphite, the total heat of transformation (2) might be endothermic, also when the homogeneous process in the direction of the arrow was *exothermic*.

In the opposite case, however, the reaction in the homogeneous phases in the direction of the arrow would certainly be endothermic.

Thus we come to the conclusion that the case of inverse deposition of solid phases supposed here is possible, when the conversion :



taking place in the homogeneous phases between the points  $g$  and  $b$  has become less *greatly endothermic or exothermic*.

As is known, a change in the heat-effect with the temperature is a phenomenon of general occurrence, which owes its origin to the circumstance that the specific heat is a function of the temperature. Repeatedly great changes of the heat of reaction with the temperature have been observed, so much so that a reversal of the sign of the heat took place, from which accordingly follows, that the possibility of the here supposed case was to be expected on the ground of our present knowledge.

Now we shall proceed to the discussion of the other three-phase lines, which likewise start from the two quadruple points  $b$  and  $g$ .

In the first place a three-phase line for  $\text{C} + \text{Fe C} + \text{G}$  still starts from the point  $b$ . To determine the direction of this curve we may make use again of VAN DER WAALS' theory of binary mixtures.

If we denote graphite by  $S_1$  and carbide by  $S_2$ , the following relation follows from the theory mentioned for the three-phase line for  $\text{C} + \text{Fe C} + \text{G}$  :

$$T \left( \frac{dp}{dT} \right)_{S_1 S_2 G} = \frac{W_{s_1 g} - \frac{x_{s_1} - x_g}{x_{s_2} - x_g} W_{s_2 g}}{V_{s_1 g} - \frac{x_{s_1} - x_g}{x_{s_2} - x_g} V_{s_2 g}} \dots \dots (I)$$

In the quadruple point  $b$  numerator and denominator indicate the

heat-effect and the change of volume, which attends the transformation (1). If we first consider the denominator, we see that  $V_{s_1g}$  and  $V_{s_2g}$  are both negative and differ little. And as further  $x_{s_1} - x_g > x_{s_2} - x_g$ , we see immediately that the denominator will be positive.

About the numerator we know that it is negative in  $b$ , so that it follows from the sign of numerator and denominator, that  $T \frac{dp}{dT}$  is negative, and that the three-phase pressure will descend with rise of temperature, at least in the neighbourhood of  $b$ .

With a view to the further discussion it is desirable to examine the numerator somewhat more closely.  $W_{s_1g}$  and  $W_{s_2g}$  are the quantities of heat which are developed when a gr. mol. of  $S_1$  resp.  $S_2$  evaporates in an infinitely large quantity of the coexisting vapour phase. We can divide both quantities into two others, viz. into a molecular heat of evaporation and a molecular differential heat of mixing e.g.

$$W_{S_1g} = (W_{S_1g})_x + W_{g_{x_1}g}$$

The heat of evaporation  $(W_{S_1g})_x$  is negative. If now we further assume that the formation of FeC is endothermic at  $b$ , so

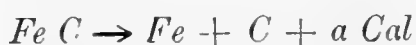


which is more probable, the heat of mixing  $W_{g_{x_1}g}$  will also be negative, so that  $W_{S_1g}$  is also negative then.

For  $W_{S_2g}$  we may write:

$$W_{S_2g} = (W_{S_2g})_x + W_{g_{x_2}g}.$$

The molecular heat of evaporation  $(W_{S_2g})_x$  is again negative. The differential heat of mixing  $W_{g_{x_2}g}$  will consist almost exclusively in the heat effect of the conversion:



which as has been indicated here, is positive at  $b$ , so that  $W_{g_{x_2}g}$  can be also positive, and  $W_{S_2g}$  negative or even positive. So we see from this how it is possible here that notwithstanding the fraction  $\frac{x_{S_1} - x_g}{x_{S_2} - x_g} > 1$  the quantity  $W_{S_1g}$  predominates in equation (I), so that the numerator is negative.

It is now clear that when on rise of temperature the heat of formation of FeC becomes smaller negative in the gas phase, and finally passing through zero, assumes a positive value, the negative



value of  $W_{s_1g}$  will continually decrease, and that of  $W_{s_2g}$  will increase. From this it follows that the numerator which is at first negative, will likewise pass through zero and become positive. This happens before the second quadruple point  $g$  has been reached, for in that point the numerator must be positive already. So we arrive at the conclusion that  $T \frac{dp}{dT}$  for the three-phase line  $S_1 + S_2 + G$  starting from  $b$  is negative, then passes through zero, and has a positive value in  $g$ , so that the said three-phase line, which joins the two quadruple points  $b$  and  $g$ , possesses a minimum pressure, as is indicated in fig. 3.

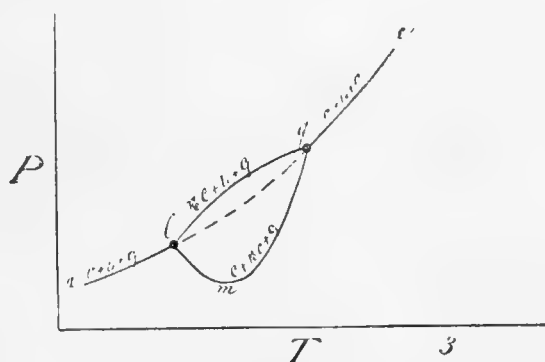


Fig. 3.

The considerations given here may be directly applied to the fourth three-phase line of the mentioned two quadruple points, viz. to that for  $S_1 + S_2 + L$ . The equation, which we want in this case, is quite analogous with equation (1), and we need only substitute the letter  $l$  for  $g$  to obtain the true relation, so:

$$T \left( \frac{dp}{dT} \right)_{S_1 S_2 L} = \frac{W_{s_1 l} - \frac{x_{s_1} - x_l}{x_{s_2} - x} W_{s_2 l}}{V_{s_1 l} - \frac{x_{s_1} - x_l}{x_{s_2} - x} V_{s_2 l}} \dots \dots (II)$$

The discussion of the numerator is perfectly identical with that just given, but now the denominator requires further consideration.

We were convinced that  $V_{S_1g}$  and  $V_{S_2g}$  are negative, but about the quantities  $V_{S_1l}$  and  $V_{S_2l}$  we must make the following remarks. The known increase of volume, which takes place in iron-carbon mixtures on solidification leads us to expect that this property is to be attributed to the presence of the component carbon, which behaves probably in the same way as the substance water. In consequence of this not only carbon, but also carbon-compounds will exhibit increase of volume on solidification, specially when the compound

contains comparatively much carbon, whereas compounds with a smaller percentage of carbon will probably behave like iron.

If we now assume that  $V_{S_1l}$  and  $V_{S_2l}$  are both positive, then it is possible that the denominator of equation (II) is negative, and the numerator also having a negative value at  $b$ ,  $T\left(\frac{dp}{dT}\right)_{S_1S_2L}$  will begin in this case in  $b$  with a positive value. In the second quadruple point  $g$  the numerator is positive, as I showed before, and consequently  $T\left(\frac{dp}{dT}\right)_{S_1S_2L}$  will be negative.

Reasoning in the same strain as before in the discussion of the three-phase line for  $S_1 + S_2 + G$  it follows that the three-phase line for  $S_1 + S_2 + L$  will possess a pressure maximum, as has been schematically represented in fig. 4.

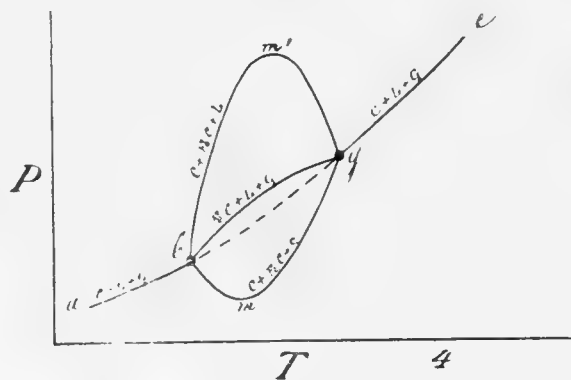


Fig. 4.

When on the other hand  $V_{S_1l}$  is positive and  $V_{S_2l}$  negative, the denominator has a positive value, and  $T\left(\frac{dp}{dT}\right)_{S_1S_2L}$  will consequently be negative at  $b$  and positive at  $g$ , in consequence of which the  $P,T$ -figure becomes as it has been drawn in fig. 5.

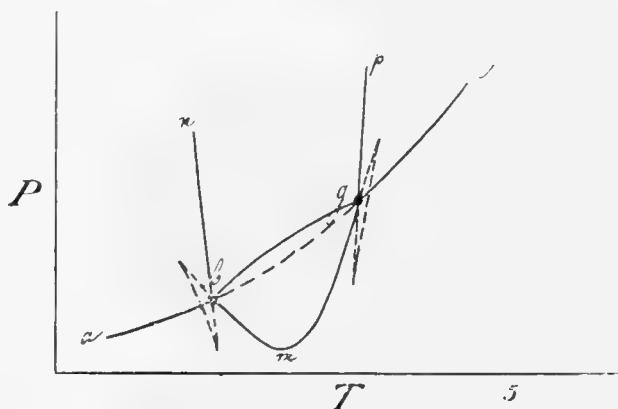


Fig. 5.

A metastable minimum cannot occur here, because the three-phase lines for  $C + FeC + G$  and for  $C + FeC + L$  pass continuously

into each other by means of two cusps in the way indicated in fig. 5<sup>1</sup>). Finally it may still be pointed out that it is possible that in the last case the denominator passes through zero, which would bring about a combination of the figures 4 and 5.

If we now apply the results obtained here to our original case indicated in fig. 1, we arrive easily at the correct result, when we omit in our thoughts first the three-phase line for  $\text{FeC}_2 + \text{L} + \text{G}$ , and then that for  $\text{FeC} + \text{L} + \text{G}$ . We then get two intersecting figures, in which we can easily distinguish the stable equilibria from the metastable ones.

Fig. 6 gives the  $P, T$ -projection for the case that we have twice the same type as fig. 4.

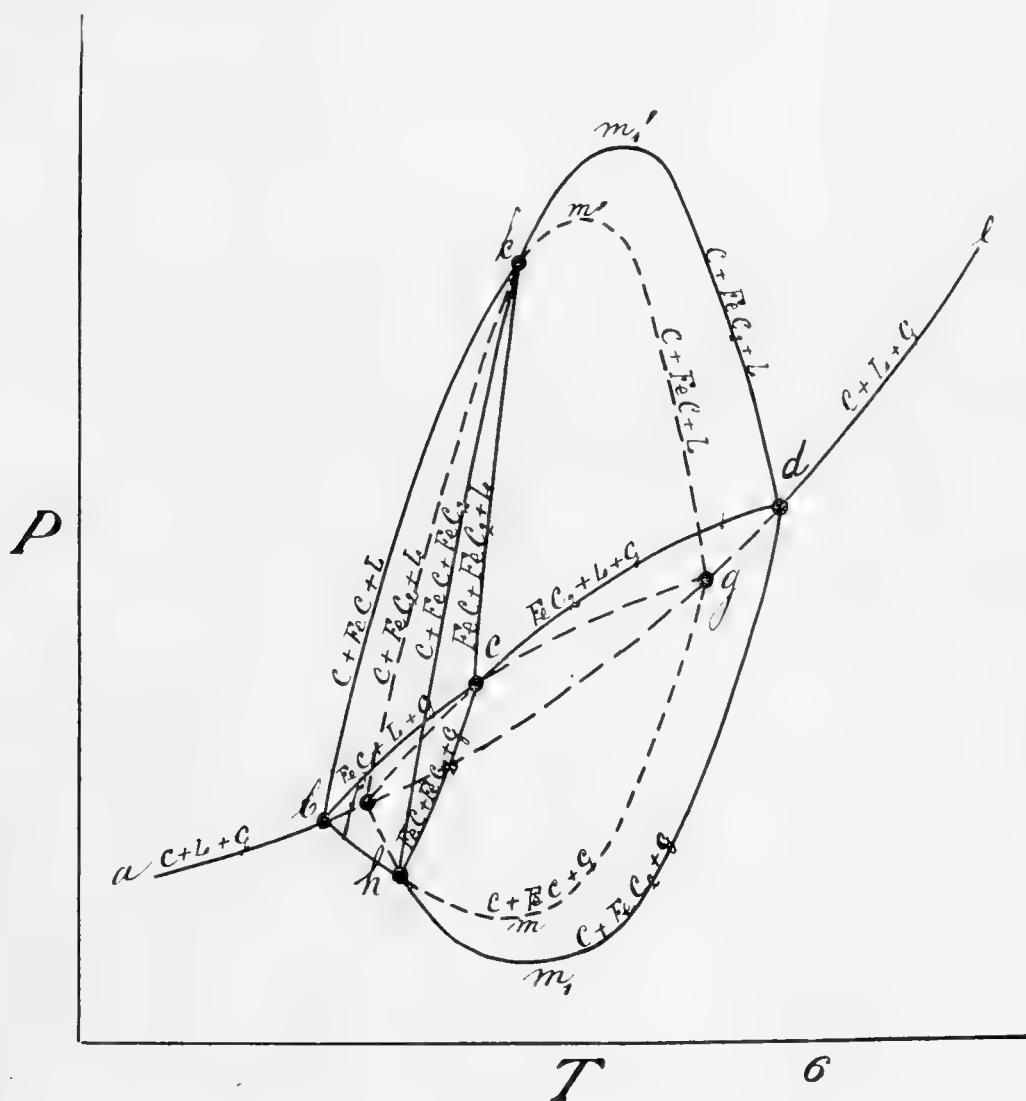


Fig. 6.

The three-phase lines for  $\text{C} + \text{FeC} + \text{G}$  and  $\text{C} + \text{FeC}_2 + \text{G}$  intersect in  $h$ , where a new quadruple point is formed, from which two more three-phase lines start, viz.  $hk$  for  $\text{C} + \text{FeC} + \text{FeC}_2$ , and  $hc$  for  $\text{FeC} + \text{FeC}_2 + \text{G}$ . The point  $k$  is the point of intersection for the three-phase line  $bm'g$  for  $\text{C} + \text{FeC} + \text{L}$ , and of the three-

<sup>1</sup>) Comp. the paper of Dr. SCHEFFER, These Proc. p. 389.

phase line  $fm_1'd$  for  $C + FeC_2 + L$ , and so this latter three-phase line, which starts from the metastable quadruple point  $f$ , becomes stable at  $k$ , and then after having reached a maximum, it runs to the quadruple point  $d$ . So the point  $k$  is also a quadruple point, where besides the two mentioned three-phase lines, two others meet viz. the three-phase line for  $FeC + FeC_2 + L$  and that for  $C + FeC + FeC_2$ . It is clear that the situation could also have been such that the three-phase line for  $C + FeC + L$  possessed a stable maximum, but this does not give rise to essential modifications. If we examine a combination of twice the type of fig. 5, the case is less remarkable.

*Anorganic Chemical Laboratory*

*Amsterdam, September 8, 1912. of the University.*

**Physics.** — “*On the system ether-water.*” By Dr. F. E. C. SCHEFFER.  
(Communicated by Prof. J. D. VAN DER WAALS).

1. In his Thesis for the doctorate (1912) Dr. REEDERS described a number of experiments which were undertaken with a view to the experimental realisation of the phenomenon of double retrograde condensation, which had been predicted by Prof. VAN DER WAALS. Both the systems which were used for this investigation, carbonic acid and urethane, resp. carbonic acid and nitrobenzene exhibited three-phase pressures, which at the same temperature, were lower than the vapour pressures of the carbonic acid. In neither of the systems the direct observation of the said phenomenon has been possible. In my opinion Dr. REEDERS justly ascribes the failure of this observation to the fact that the difference in volatility of the components of both systems is so great that the vapour phase under three-phase pressure practically consists of pure carbonic acid, and consequently the quantity of the liquid layer, poor in carbonic acid, which is formed during the retrograde condensation, is so small that it escapes observation. The critical points of the upper layer lie for both systems at concentrations which are smaller than 2 mol. percentages of the least volatile substance, and hence the concentration which is to present the double retrograde condensation contains still less of the second component.

When Dr. REEDERS told me his results a long time before the publication of his Thesis for the Doctorate, it did not seem impossible to me that a system, in which the volatility of the components

differs less, might offer a greater chance to the realisation of the said phenomenon. Such systems, however, are pretty rare. For "normal" substances such a behaviour will probably seldom occur. The system ether-water, on the other hand, which as appears from KUENEN's observations, possesses three-phase equilibria which extend to the critical neighbourhood of the ether, satisfies the requirement that the vapour under three-phase pressure contains an appreciable quantity of the least volatile component, in casu the water, the vapour tension of the water amounting to about 14 atms. at the critical temperature of ether (critical pressure 36 atms.). That this system differs from those used by REEDERS in this that the three-phase pressure lies higher than the pressure of saturation of the two components at the same temperature need not interfere with the appearance of the phenomenon. Therefore I carried out some experiments about a year ago with a view of examining whether double retrograde condensation can be observed in the system ether-water. However, this system too appeared unsuitable for the observation. It is true that the critical point of the upper layer lies at a concentration of about 30 mol. % water, and that it is therefore not so one-sided as for the mentioned systems of carbonic acid, but an altogether different difficulty prevents the observation, viz. the invisibility of the lower layer for comparatively small quantities. So after some futile attempts I discontinued the observations with this system. Hence a direct observation of the phenomenon in question has not succeeded as yet, and will, it seems to me, be always attended with great experimental difficulties.

2. Of late attention has been drawn to the system ether-water in consequence of an investigation by Prof. VAN DER WAALS. In his 17th contribution to the theory of binary mixtures VAN DER WAALS discusses this system fully as an example of that series of systems for which under three-phase pressure the concentration of the vapour phase lies between that of the two coexisting liquids. As far as the system ether-water is concerned, this investigation led to a number of conclusions, some of which could be experimentally tested through the investigations mentioned in § 1, as was already stated by Prof. VAN DER WAALS in the cited paper. As it was, however, of importance to examine this system more closely with a view to the remaining conclusions, I have taken up again the interrupted investigation. In the following pages I intend to discuss the results obtained for so far as they are necessary as a test of the above-mentioned conclusions.

### 3. *Preparation of the mixtures, method of observation.*

Commercial ether (*Pharmacopœia Néerlandica*) was twice shaken with strong sulphuric acid, and dried first on sodium sulphate, then on sodium. It was preserved in this condition; for the preparation of every mixture part of this stock was distilled. As second component distilled water was used. For the preparation of the mixtures use

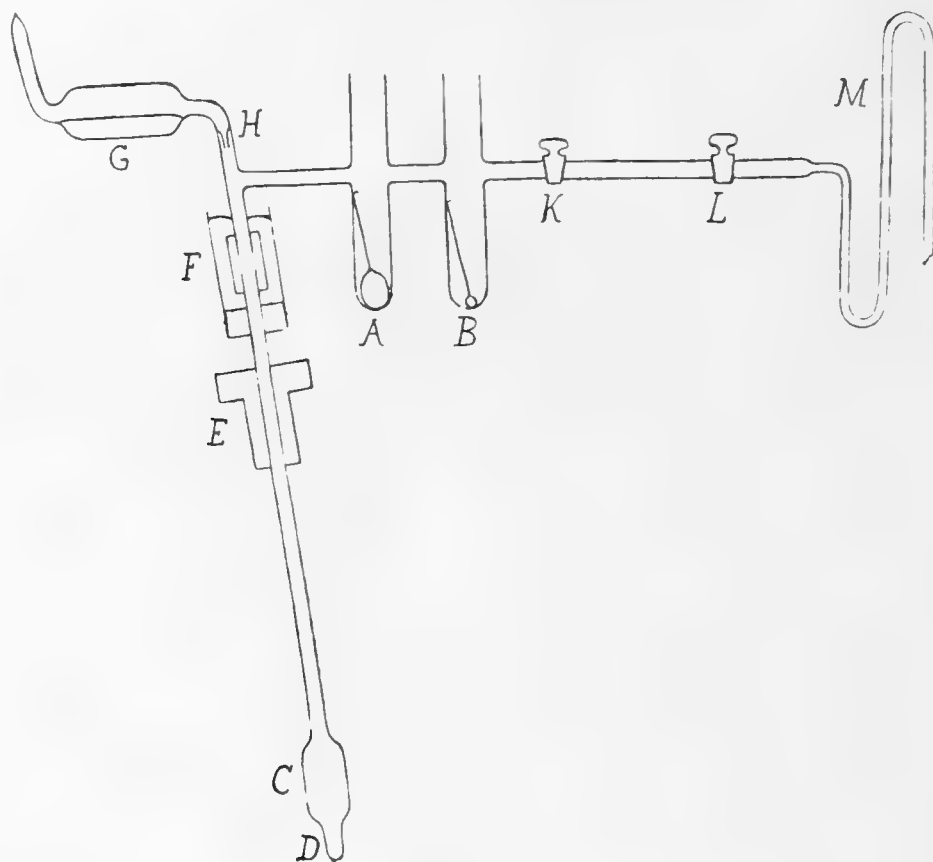


Fig. 1.

was made of the apparatus represented in fig. 1. Each of the components was weighed in a small thin-walled glass bulb provided with a capillary stem, and put in the tubes *A* and *B*, which were then fused to at their tops. The Cailletet test tube of combustion glass *ED* was connected with the filling apparatus in reversed position by means of a rubber tube surrounded by a mercury joint. Near its end *D* the tube is widened to enlarge the volume, which enabled us to perform the experiments with a comparatively large quantity of substance. This was necessary, because exclusively concentrations on the ether side were examined for this investigation; if a Cailletet tube of the ordinary shape had been used the quantity of water used would have been too small for accurate observations.

The part of the apparatus represented in fig. 1 was connected by means of the glass spiral *M* with two tubes with cocoa-nut carbon, a Geissler tube, and a water-jet pump, which served to

bring about a sufficient vacuum<sup>1</sup>). When the whole apparatus had been exhausted, the bulb with water was broken by cooling with carbonic acid alcohol, that with ether by heating, and the contents of both were condensed in *C* and *D* by means of liquid air. The air dissolved in the liquid in the bulbs could then be removed by the cocoa-nut carbon. Then the mercury which had been boiled in vacuo was conveyed from *G* in small drops through the constriction *H* into the Cailletet tube, which was then screwed into the pressure cylindre in the known way after having been separated from the filling apparatus at *F*.

In some experiments the stem of the bulb filled with water was put into the opening of the plug of cock *K*, and broken after the evacuation of the apparatus by rotation of *K*. This method of working proved very convenient for the realisation of concentrations of definite amount. Then there was no necessity for the bulb to be filled so far with water as is necessary for bursting in consequence of solidification and the weighing of a definite quantity of substance was rendered a great deal easier thereby.

At last the Cailletet tube was surrounded with a jacket, in which nitrobenzene was electrically heated till it boiled under varying pressures<sup>2</sup>).

#### 4. *Discussion of the results.*

In the cited paper the shape of the plaitpoint curve in its  $T, x$ -, and its  $P, T$ -projection was examined by Prof. VAN DER WAALS. It then appeared that after some modification fig. 43 of the series of contributions mentioned can account for the phenomena which appear

1) Cf. e.g. These Proc. XIII p. 831 and fig. I on p. 830.

2) To obtain constant temperatures I made use of a steam-jacket, which is different from the one generally used. A wide tube is provided with a smaller one on either side which are closed with rubber stoppers prepared for high temperatures. On the constriction at the bottom rests an inner tube, which ends about 10 cm from the upper constriction. The stopper on the bottom side has one perforation for the Cailletet tube, which is entirely inside the inner tube, two for the supply of the electric current, and an aperture through which a tube is put for sucking up and letting out the boiling-liquid. The heating is effected by means of a nickeline wire adjusted in the inner tube and wound spirally. The boiling liquid rises in the inner tube, condenses in the upper part of the outer tube, and flows down in it. In the inner tube two branch apertures have been made close to the bottom to keep the liquid at the same level inside and outside the inner tube. A glass tube through the stopper at the upper end brings about the connection with water jet pump, manometer, pressure regulator etc. If we proceed in this way there is no difficulty whatever in keeping the temperature constant for any length of time.

in the system ether-water. In fig. 43 the case has been drawn that the three-phase line would just terminate at the minimum critical temperature; in the 17<sup>th</sup> contribution, however, it is pointed out that this end-point of the three-phase line, which we will designate by the name of "critical endpoint" in our further considerations, may occur both on the branch  $AQ_2$  and on the branch  $Q_2P_{cd}$ .

Hence we shall have to distinguish three cases as regards the relative situation of the critical end-point and the minimum critical temperature, viz.:

1. If the critical end-point lies on the branch  $AQ_2$ , the critical line in its  $P, T$ -projection will have the shape as has been drawn in fig. 51 of the paper that has already been cited several times. Then the minimum critical temperature is found in the metastable region, and cannot be experimentally realized except by the appearance of phenomena of retardation.

2. If the three-phase line terminates exactly in the point  $Q_2$  (fig. 43), the minimum critical temperature would occur just on the boundary of metastable and stable phases, and so it could be demonstrated by experiment. The  $P, T$ -projection for this case has been represented in fig. 50.

3. If lastly the three-phase line terminates on the branch  $Q_2P_{cd}$ , the critical end-point lies on the righthand of the minimum critical temperature. Accordingly the latter, if really present, will lie in the stable region, and might be found experimentally. If, however, it is not present, it might be imagined to lie outside the figure, and the plaitpoint curve on the side of the ether would have to exhibit the tendency to this minimum. At last as transition case we might still suppose that the minimum critical temperature would just coincide with the critical point of ether, and that therefore it could just be still demonstrated. As far as the  $P, T$ -projection is concerned, the presence or absence of the minimum critical temperature would have to manifest itself in a strong negative rise with vertical tangent, resp. in a very strong positive rise on the ether side.

From the above-cited experiments by KUENEN it may be already inferred that the system ether-water is a case as mentioned under 3. The critical temperature of the upper layer lies, namely, at higher temperature than the critical temperature of pure ether. So the critical end-point lies on the ascending branch in the  $T, x$ -projection.

In the cited treatise case 3 has therefore been fully examined, and Prof. VAN DER WAALS arrives at the conclusion that it is possible that the three-phase line before terminating on the critical line, first



intersects it in its  $P, T$ -projection. With regard to this last case again three cases may be distinguished. We may, namely, imagine that the three-phase line without previous intersection terminates on the critical line, that intersection takes place before this end-point (see fig. 48), and thirdly that the intersection takes place exactly in the end-point, i.e. that in the critical end-point the three-phase line touches the critical line (fig. 49). This last case is again to be considered as the transition case between the two first-mentioned ones.

5. To enable us to decide which of the possible cases discussed in the preceding paragraph presents itself in the system ether-water, the  $P, T$ -projections of the plaitpoint line and the three-phase line had to be experimentally determined. For it is possible to derive from the situation of the plaitpoint line whether or no a minimum critical temperature occurs (vertical tangent), and from the relative situation of the said lines a conclusion may be drawn as to whether or no an intersection occurs. So the determination of the  $P, T$ -projections of the two lines might suffice; the three-phase line can be determined by means of one mixture, provided it do not possess a concentration that lies too much on one side. For the determination of the critical line the  $T_k$  and  $P_k$  found for different mixtures should be combined together to one line. So for every mixture practically nothing but the critical phenomenon need be observed, and of a single one the three-phase line in the neighbourhood of the critical end-point.

However, I have not been satisfied with this. To obtain as much certainty as possible I have observed part of the three- and two-phase equilibria of every mixture. The great advantage yielded by these observations, is the following. If a mixture should contain a slight quantity of admixtures, and the presence of air is the most probable, this mixture would bring about an error in  $T_k$  and  $P_k$ , and so it might furnish a point which might cause the course of the critical line to deviate from the correct one. In the determination of the three-phase pressure, which must show the same value for all the mixtures used, we have, however, a criterion of purity. With none of the mixture, for which this test could be applied, a deviation was found exceeding 0,1 atmosphere.

But besides this, the observation of the two-phase equilibria furnished another advantage. We want to decide, among others, whether intersection takes place between the three-phase line and the critical curve. If we now put the case that this intersection really occurs, the part of the critical line between the point of intersection in question and

the critical end-point lies at higher pressure than the three-phase line. So two-phase equilibria must be possible at these temperatures between liquid rich in ether and vapour at pressures higher than the three-phase pressure. If, therefore, only one point of end-condensation of the ether layer was found to lie higher than the three-phase pressure at the same temperature, the intersection would have been proved. So we see that in the observation of the two-phase equilibria we may find a second decision on the presence or absence of the point of intersection in question.

Now what concerns the observation of the two-phase equilibria we have already seen in § 1, that the liquid which is rich in water is sometimes not observable in the mixtures. This, however, does not

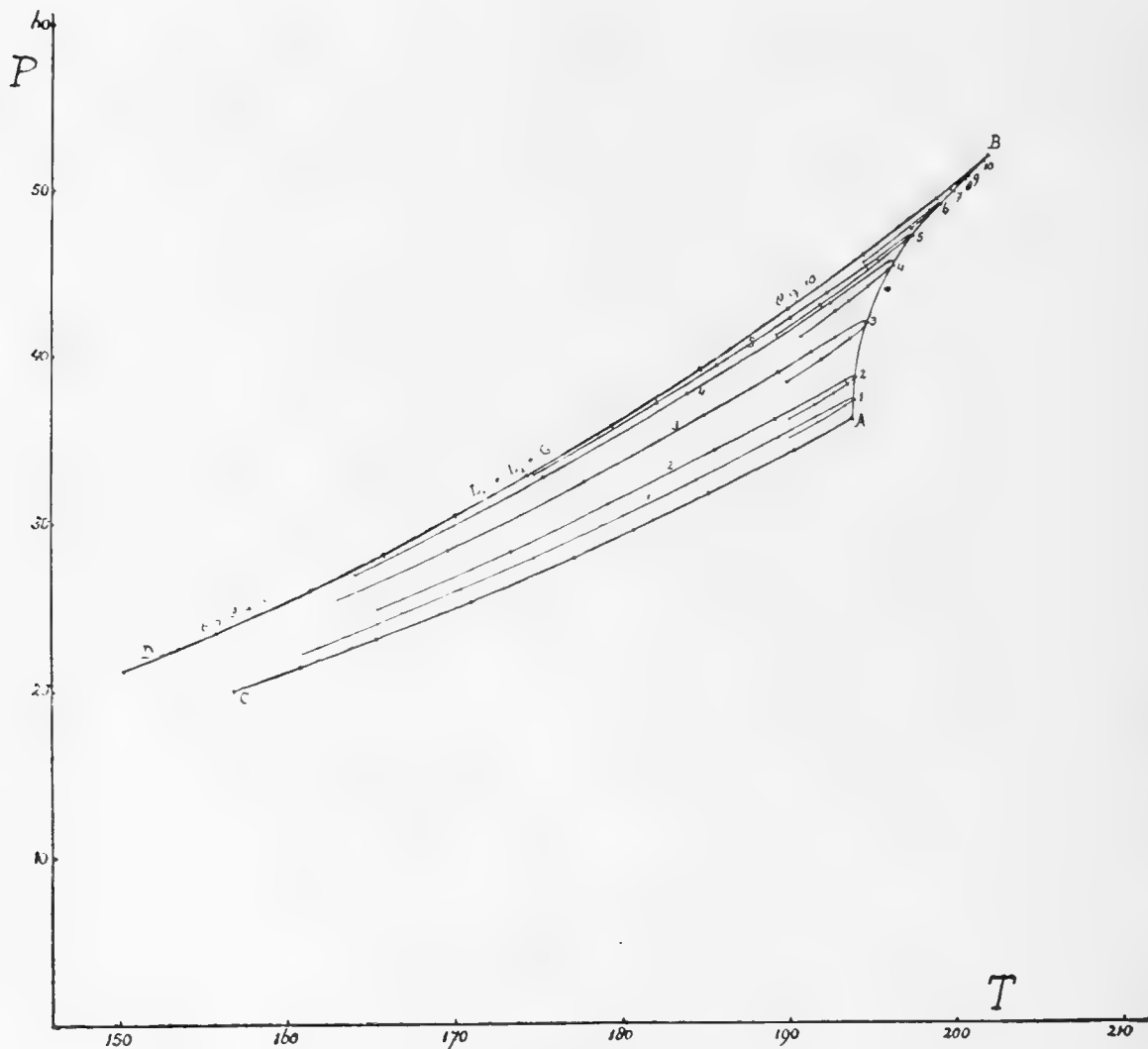


Fig. 2.

affect the decision in question. For every mixture I determined the initial and the final condensations of the ether layer in the neighbourhood of the critical temperature. If in one of the two a layer is present, visible or invisible, which is rich in water, the pressure must be the same as the three-phase pressure. Now it follows from



the observations given in figure 2 and table I of pure ether of the three-phase pressure determined with a mixture of about equal quantities by weight, and of some ten mixtures of the concentration given in the table, that not a single end-condensation of the ether layer can be realized which took place at higher pressure than the three-phase pressure. This shows us in an indirect way, what we also see directly from the locus of the plaitpoints, that there is no intersection between plaitpoint line and three-phase line. The relative position of the two lines is, however, such that we are here quite in the neighbourhood of the above-mentioned transition case. The inclination of the two lines in the critical end-point differs so little that we may practically speak of contact here. In the  $P, T$ -projection the lines of the initial and final condensation of the ether layer have been indicated by the same numbers as the corresponding mixtures in the adjoined table.<sup>1)</sup> It is clear that the mixtures 6, 7, 8, 9, and 10 in the neighbourhood of  $160^\circ$  have yielded the three-phase line as end-condensation. In ascending order this was the case up to higher and higher temperature. For the mixtures 1 to 5 the end-condensation pressure was lower than the three-phase pressure over the whole range of temperature; hence there was no question of the occurrence of three-phase equilibria with these mixtures. The intersection of the line of the end-condensations and the three-phase line must be looked for here at lower temperature.

It is, moreover, clear, from figure 2 that the critical line at the critical point  $A$  of the ether rapidly proceeds to higher pressure, as Prof. VAN DER WAALS anticipated. Whether the inclination is infinitely great or very great in the direct neighbourhood of  $T_k$  of ether, could not be ascertained. Also in this respect we may again speak of a transition case for this system. For we cannot state with certainty whether the minimum critical temperature lies in the figure or on the axis, or whether it would lie just outside the figure. The last seems, however, the most probable from the given observations.

When the plaitpoint line is considered in its other projections, it appears that in the  $T, x$ -projection the inclination on the ether side is very slight, almost zero, and that it continually increases up to the critical end-point on increasing concentration. In the graphical representation the  $P, x$ -projection appears to deviate very little from a straight line.

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<sup>1)</sup> In the table the critical data have been given in bold type, above them we find the values of the end-, below them those of the begin-condensations of the ether layer.

If we finally consider the relative situation of the phases on the three-phase line, it appears from what precedes that the vapour phase lies between the coexisting liquids up to the highest temperature, that the vapour branch, however, closely approaches the branch of the liquid rich in ether already before the critical end-point. It is in agreement with this that a  $P,x$ -section brought through the  $P,T,x$ -surface e.g. for the critical temperature of ether yields two curves which show decreasing values of  $\frac{dP}{dx}$  starting from the critical pressure of ether, that the intersection with the three-phase line, however, appears just before the maximum pressure is reached, at which the concentrations of liquid and vapour would become the same.

So in the system ether-water the minimum critical temperature predicted by Prof. VAN DER WAALS lies in the immediate neighbourhood of the axis, and the remarkable point of intersection at the critical end-point.

I intend to repeat this investigation for another system hoping that I shall be able to demonstrate both peculiarities experimentally when the situation is a less one-sided one.

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*Amsterdam, Sept. 13 1912.*

**Chemistry.** — “*On quadruple points and the continuities of the three-phase lines.*” By DR. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

1, In a previous paper<sup>1)</sup> I examined the continuous connection of the three-phase lines, which occur in BAKHUIS ROOZEBOOM's spacial figure on the most simple suppositions. It then appeared that the three-phase lines  $S_A + S_B + L$  and  $S_A + S_B + G$  pass continuously into each other, and that in the  $P,T$ -projection this transition takes place by means of a partly metastable, partly unstable curve with two cusps, in both of which two three-phase branches touch. I have now extended this investigation to the other quadruple points which can occur in binary systems; I have, however, postponed the publication of it for a long time, because the phenomena which present themselves in the most interesting case, are much more complicated than in the above mentioned case, and a full description would require a great many intricate figures. Without treating the cases

<sup>1)</sup> These Proc. 1910, p. 158.

fully I have, however, managed to give a survey of the phenomena which in general present themselves in quadruple points. It seems to me that the construction of the figures referring to a definite case will not present any difficulties, if this survey is consulted.

In the first place I will assume in the following considerations that continuity only takes place between liquid and gas phases. So I preclude an eventually present continuity between solid and fluid. If it should appear that VAN LAAR'S theory, which leads to this continuity, is valid, this transition will also have to be reckoned with for a complete treatment. On the appearance of a quadruple point  $S_1 + S_2 + S_3 + S_4$  the four solid phases could then pass continuously into each other. Until, however, the existence of the continuity in question shall have been experimentally realized, it seems better to me not to take it into account to prevent our entering into an elaborate consideration of a great many cases which may appear later on to be physically impossible.

In the second place I exclude a continuity between solid phases. Their occurrence has indeed been ascertained, but until certainty has been obtained as to how the crystallographic orientation in the equation of state of the solid substance is to be taken into account, it seems impossible to me to obtain certainty about the connection of the three-phase lines in consequence of this continuity.

If we now consider that in a binary system unmixing in the gaseous state has never been found as yet, and never more than two simultaneous liquid layers, it appears that in all six different quadruple points can occur:

1.  $S_1 + S_2 + S_3 + S_4$     3.  $S_1 + S_2 + L_1 + L_2$     5.  $S_1 + S_2 + L + G$   
 2.  $S_1 + S_2 + S_3 + L$     4.  $S_1 + S_2 + S_3 + G$     6.  $S + L_1 + L_2 + G$

In the quadruple points **1**, **2**, and **4** no continuities can appear between the three-phase lines, in which liquid and gas phases participate. Of the three cases **3**, **5**, and **6**, which accordingly remain for our consideration, the case **5** has already been fully examined in the cited paper.

Case **3** only differs slightly from **5**. In the quadruple point **3** the three-phase lines  $S_1 + S_2 + L_1$ ,  $S_1 + S_2 + L_2$ ,  $S_1 + L_1 + L_2$  and  $S_2 + L_1 + L_2$  occur, of which only the two first are in continuous connection with each other. It is easy to see by the aid of the  $V, x$ -projection, that this connection again takes place by means of an unstable branch with two cusps in the  $P, T$ -projection, just as this

was shown before for the case **5** with regard to the three-phase lines  $S_1 + S_2 + L$  and  $S_1 + S_2 + G$  <sup>1)</sup>).

If, however, we compare the three-phase lines  $S_1 + L_1 + L_2$  and  $S_2 + L_1 + L_2$  of case **3** with the corresponding lines  $S_1 + L + G$  and  $S_2 + L + G$  of case **5**, it is clear that in the latter case the two lines terminate in the melting-points of the two components, at least if we have a case of the ordinary spacial figure. In case **3** on the other hand, the binodal line of the two liquids can be an entirely closed curve with two plaitpoints. Each of the three-phase lines  $S_1 + L_1 + L_2$  and  $S_2 + L_1 + L_2$  will then possess two critical end-points in the  $P, T$ -projection. Yet this difference between the cases **3** and **5** is not so great as one would be led to expect at first sight. The occurrence of critical end-points is not confined to the case **3**; also in case **5** it is possible that the three-phase lines  $S_1 + L + G$  and  $S_2 + L + G$  do not reach the melting-point, but come into contact with a critical line. This case, which is pretty well the prevailing one in case **3**, has been shown by SMITS for case **5** in the system ether-anthraquinone.

## 2. *The quadruple point $S + L_1 + L_2 + G$ .*

So we have seen that the quadruple points **3** and **5** give rise to analogous phenomena; the only remaining case **6**, however, deviates from what we discussed in many respects. Where in the quadruple points **3** and **5** continuity is always only possible between two phases we have three phases  $L_1$ ,  $L_2$  and  $G$ , in the quadruple point **6**, which all three may pass continuously into each other. So the phenomena become more complicated here, and it is already a priori clear that the connection between the three-phase lines may take place in different ways. What cases we have to distinguish for this quadruple point can be easily derived from Prof. VAN DER WAAALS' investigations on unmixing. It is known that the critical line can present very different shapes when a longitudinal plait exists on the  $\psi$ -surface.

In the first place we may imagine that at low temperature solely a transverse plait occurs on the  $\psi$ -surface, that on rise of temperature a longitudinal plait is formed (inside the transverse plait), that on further rise of temperature it makes its way outside the transverse plait, and that it afterwards again retreats inside the plait, and disappears at a temperature which lies lower than the lowest critical temperature of the transverse plait. This case, to which we shall

<sup>1)</sup> Cf. also § 3.

refer as the first in our further considerations, yields a critical line, which consists of two entirely detached portions, one of which, lying at high temperature, presents the normal shape, and the other is in the  $P,T$ -projection a closed figure with two heterogeneous double plait-points, which represents the locus of the critical points of the longitudinal plait.

In the second place it is possible that the longitudinal plait, which has got outside the transverse plait in the same way as above, continues to exist far above the temperature at which the transverse plait gets detached on one of the two sides. Then a transition takes place at a certain temperature in the connection of the plaits; the longitudinal plait, which was entirely closed at low temperature, then merges into a part of the transverse plait, while simultaneously the portion of the transverse plait on the side of the component with the lower critical temperature gets isolated, and retreats inside the former at rise of temperature, and disappears. This case is referred to as the second in what follows.

I have now examined the question what phenomena may appear, when a tangent plane for solid-fluid is rolled over the  $\psi$ -surfaces in question, and it has appeared to me that the behaviour in both cases can be ascertained by a comparatively simple train of reasoning. In these considerations I have confined myself to those cases, for which only the components occur as solid substances.

### 3. *The first case.*

When we consider the case that was called the first in the preceding paragraph, we can get a survey of the phenomena by means of figure 1. In this figure it has been assumed that  $(dp/dx)_v$  is always positive, in other words that we are in the lefthand part of the isobaric figure. The longitudinal plait here possesses two critical points  $P_1$  and  $P_2$ , where contact takes place with the spinodal line. Further only the liquid binodal line has been drawn of the transverse plait; the vapour branch, which lies at large volumes has been omitted in the diagram; it possesses a ridge, the two end-points of which indicate the phases coexisting with  $A$  and  $B$ . About the relative situation of longitudinal and transverse plait we know that at low temperature the longitudinal plait lies entirely inside the transverse plait, at higher temperature the former passes the border of the transverse plait, and at still higher temperature it retreats again inside the latter. In this temperature range the transverse plait covers the whole width of the figure, as we remain all the time below the critical temperature of the components.



We shall now imagine that a tangent plane for solid-fluid rolls over the  $\psi$ -surface, and we choose as solid substance the first com-



Fig. 1.

ponent. At very low temperature the curve which is described by the tangent plane on the  $\psi$ -surface, will lie entirely on the right-hand side of the figure. So it will not come in contact with the longitudinal plait, if it should be present already. This condition has been represented by the curve *a* in figure 1; it intersects the binodal of the transverse plait, and this point of intersection indicates the liquid of the three-phase equilibrium  $S + L_2 + G$  (we denote by  $L_2$  the liquids lying on the righthand of the longitudinal plait). Now on rise of temperature the possibility presents itself that the binodal solid-fluid comes in contact with the longitudinal plait. If this is the case contact will take place, and this can happen nowhere else than in the plaitpoint. This is easy to see, as in case of contact in another point of the longitudinal plait a second liquid would have to coexist with the solid substance, and so no contact, but intersection would have to take place. This condition of contact has been represented by curve *b*. So the fluid phases coexisting with solid yield a line *b*, which passes through the stable plaitpoint of the longitudinal plait, and intersects the transverse plait in two points, of which again only the liquid point has been indicated in fig. 1.

Then at higher temperature an intersection follows in four points. Two points of intersection with the longitudinal and two with the transverse plait then lie on the line solid-fluid; so at this temperature there are two stable three-phase equilibria  $S + L_1 + L_2$  and

$S + L_2 + G$  (line  $c$ ); the equilibrium  $L_1 + L_2 + G$  is still metastable. This condition continues to exist till the line for the fluid phases coexisting with solid gets into contact with the liquid branch of the transverse plait in A, and then also passes through the righthand cusp in the vapour branch of the transverse plait (line  $d$ ). This is followed by a range of temperature, in which six points of intersection with the transverse plait, and still two with the longitudinal one occur. At these temperatures five three-phase equilibria then appear in all. This range terminates at the temperature of the curve  $f$ , where again contact with the liquid branch of the transverse plait is found (in B), and the line for fluid by the side of solid passes through the lefthand cusp of the vapour binodal curve. In this temperature range we find the quadruple point, the behaviour of which is given by the curve  $e$ . Above this range of temperature four points of intersection again occur, till the temperature is raised to that of  $g$ , where contact with the longitudinal plait takes place. Then eight points of intersection again follow, six of which, however, now lie on the longitudinal plait. This continues to be so till the condition  $h$  is reached, above which again two intersections with the longitudinal, and again two with the transverse plait take place (curve  $i$ ). At last in  $k$  the temperature is reached at which contact in the hidden plaitpoint  $P_2$  takes place. At still higher temperature

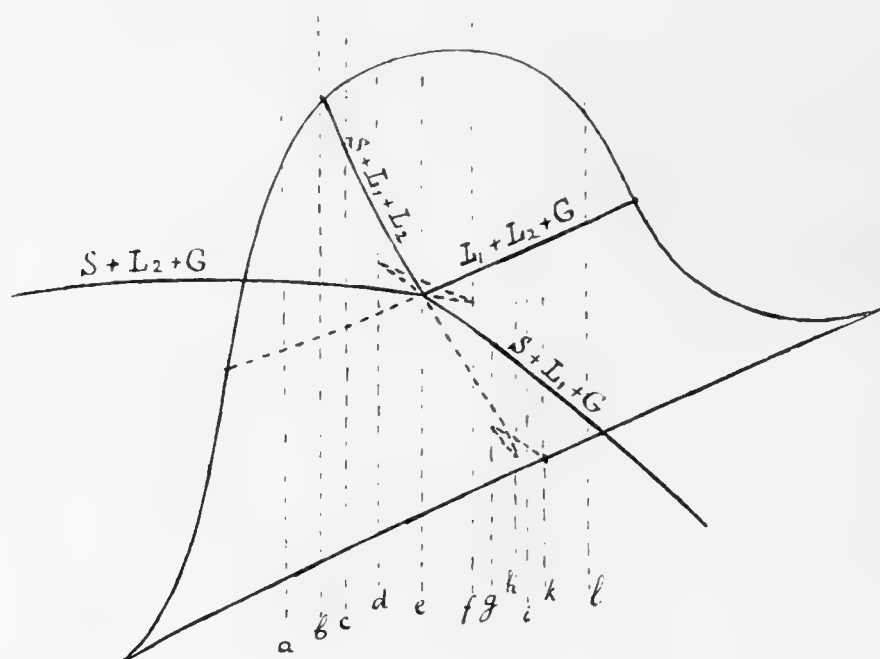


Fig. 2.

there is no longer contact of the fluid line with the longitudinal plait, and the latter will recede within the transverse plait.

After this discussion it will be easy to construct the  $P, T$ -projection of the three-phase lines, which has been given in fig. 2. The tem-

peratures for which the intersections in fig. 1 were studied, have been indicated in fig. 2 by the same letters. The three-phase line  $L_1 + L_2 + G$  retains therefore the shape which it has when no solid substance occurs; one part has, however, become metastable here. Just as the line  $L_1 + L_2 + G$  the three-phase line  $S + L_1 + L_2$  possesses two plaitpoints, one of which is stable, and the other metastable or unstable. Besides the former possesses a ridge, which lies entirely in the non-stable region, the ends of which correspond with the points where the lines  $g$  and  $h$  of fig. 1 cut the spinodal curve. The two other three-phase lines  $S + L_1 + G$  and  $S + L_2 + G$  are continuously connected by means of such a ridge, the end-points of which correspond with the points  $A$  and  $B$  of fig. 1. That really ridgelike figures occur here, with contact of every time two branches in the end-points is easy to see; this will always be the case when two binodal lines touch in a point of the spinodal line (plaitpoints excepted). If we choose the temperature very little different from that at which contact takes place, then if the direction of the change of temperature has been correctly chosen, an intersection will appear of the binodals; then in the  $V, x$ -figure there are two three-phase-triangles present, the angular points of which draw near to each other on approach of the temperature of contact, and coincide when this temperature is reached. If e. g. we have the intersection of a line between  $d$  and  $e$  with the transverse plait in fig. 1, then the two phases  $L_1$ , the two phases  $G$ , and the two solid phases will coincide at a lower temperature.

Now the value for  $\frac{dp}{dT}$  for both the two three-phase equilibria is given by the equation:

$$\frac{dp}{dT} = \frac{\eta_{GL_1} - \frac{x_G - x_{L_1}}{x_S - x_{L_1}} \eta_{SL_1}}{v_{GL_1} - \frac{x_G - x_{L_1}}{x_S - x_{L_1}} v_{SL_1}},$$

in which all the quantities of the second member refer to the three coexisting phases. It is now clear that on approach of the temperature of contact the two phases  $L_1$ , the two phases  $G$ , and the two solid substances differ less and less in properties, and that at the temperature at which contact takes place, the quantities of the second member refer to identical phases. For the two three-phase branches the value of  $\frac{dp}{dT}$  becomes exactly the same at the temperature of contact, and so contact occurs.

It may be further pointed out that the value of  $\frac{dp}{dT}$  at this contact does not in general become infinitely great. This would be the case, if in the point of contact also the condition:

$$\frac{v_G - v_{L_1}}{x_G - x_{L_1}} - \frac{v_S - v_{L_1}}{v_S - v_{L_1}} = 0 \quad ;)$$

was satisfied.

It is easy to see from fig. 1 that this will not be the case in the point A.

4. In § 3 we assumed a very decided relative displacement of the fluid line with respect to the longitudinal plait for the derivation of fig. 2. It will be clear that the relative displacement of the said binodal curves can also take place in another way than that described above. If we want to ascertain how great the number of possibilities is that may occur, we should first of all bear in mind that our first assumption was, that  $\left(\frac{dp}{dx}\right)_v$  was positive on the  $\psi$ -surface. Further we took the first component as solid substance. If we now exclude the appearance of a line  $\left(\frac{dp}{dx}\right)_v = 0$ , it will be clear that we can survey all the cases if we take  $\left(\frac{dp}{dx}\right)_v$  always positive, and choose the two components as solid substances. For if  $\left(\frac{dp}{dx}\right)_v$  is negative, and the solid substance is the second component, we get the same phenomena as in the case where  $\left(\frac{dp}{dx}\right)_v$  is positive, and the first component appears as solid phase.

So if we keep  $\left(\frac{dp}{dx}\right)_v$  always positive, the situation of the longitudinal plait is always as indicated in figure 1. The differences between the cases which may occur, are accordingly caused by the fact that both components can occur as solid phase, and by the relative displacement of the solid-fluid line with respect to the longitudinal plait.

If we confine ourselves to the case that the first component is the solid phase, we see a second possibility in figure 1, if we suppose

---

1) The transformed denominator of the above expression for  $\frac{dp}{dT}$ .

that the line for solid-fluid retains its shape  $\alpha$  to higher temperatures, and that then on rise of temperature a longitudinal plait arises on the righthand of  $\alpha$ , which plait extends and overtakes the line for solid-fluid. It is clear that then contact takes place in the unstable plaitpoint  $P_2$  at low temperature, and that with rising temperature the intersections with the longitudinal plait may take place in reversed order as has been described above. In this case in opposition to fig. 2 the three-phase line  $L_1 + L_2 + G$  is stable at temperatures below the quadruple point, and at temperatures above it metastable, and the stable part of  $S + L_1 + L_2$  possesses a positive value for  $\frac{dp}{dT}$ . This, however, does not affect the connection between the three-phase lines  $S + L_1 + G$  and  $S + L_2 + G$ , and the two other three-phase lines retain their critical points just as in fig. 2.

Finally we may assume that the line for solid-fluid forces its way inside the longitudinal plait in the way represented in fig. 1 by the line  $\rho$ , and this line can again be displaced in two directions with respect to the longitudinal plait, so that either the stable or the metastable plaitpoint is situated at the lower temperature.

So we get in all four different quadruple points, when the solid substance is the first component, and as many when the second component appears as solid substance, so that we have to conclude to eight different types of quadruple points, at least if we disregard the appearance of ordinary pressure and temperature maxima, which occur, if the situation of the three-phase points satisfies the conditions:

$$\frac{\eta_2 - \eta_1}{x_2 - x_1} - \frac{\eta_3 - \eta_1}{x_3 - x_1} = 0 \quad \text{resp.} \quad \frac{v_2 - v_1}{x_2 - x_1} - \frac{v_3 - v_1}{x_3 - x_1} = 0.$$

I will not enter into the further treatment of these cases, because for all these possibilities the result already obtained in § 3 always remains intact that the two three-phase lines  $S + L_1 + G$  and  $S + L_2 + G$  are in continuous connection, and that on the two other three-phase lines two critical points occur. Nevertheless it seemed desirable to me to give a survey of these possible cases, because the appearance of these quadruple points will not be rare; they will occur in almost any system where unmixing continues to exist below the melting-points of the components.

### 3. *The second case.*

In the second case we have supposed that the longitudinal plait continues to exist to above the lower critical temperature of the transverse plait. So one of the components has then become critical,

and at these temperatures only the appearance of the other component as solid phase is possible. So again supposing  $\left(\frac{dp}{dx}\right)_v$  to be positive, only the first component can appear as solid substance because then the second component will generally possess the lower critical temperature. We know that in this case a transformation in the connection of the plaits takes place, as is indicated in fig. 3. We must now suppose that at low temperatures the behaviour does not

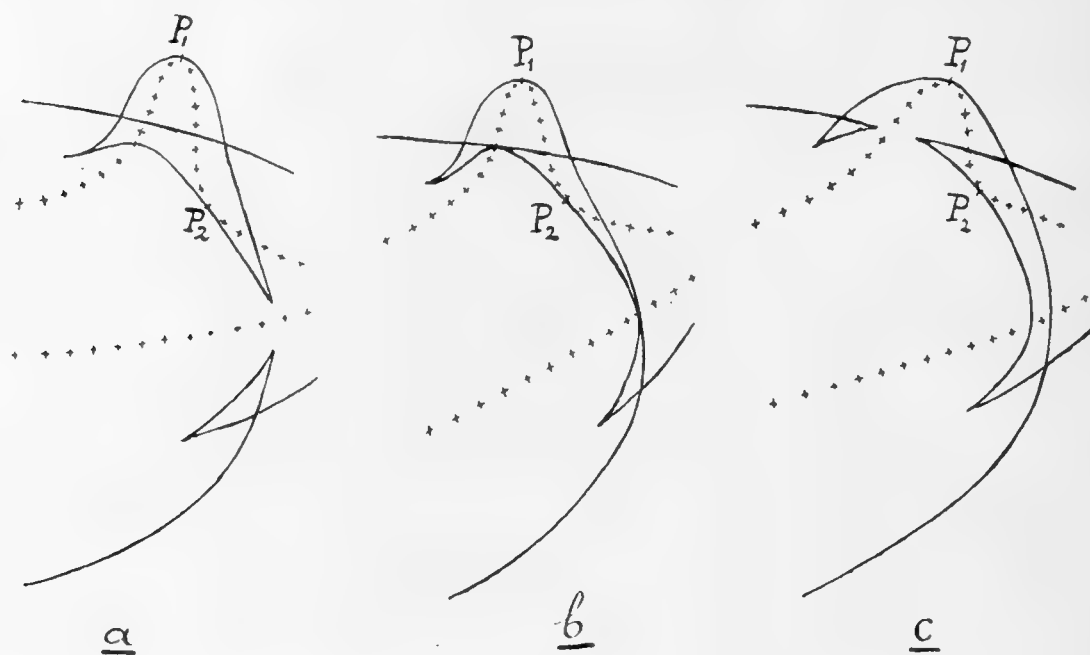


Fig. 3.

differ from what was discussed in § 3 (lines *a*, *b*, and *c* of fig. 1), that then, however, the transformation of fig. 3 makes its appearance. If this takes place before the condition *g* of figure 1 has been reached, it is clear that the liquid points of the three-phase line  $S + L_1 + L_2$  lie on the longitudinal plait at low temperature, but that when the transformation takes place the branch on which  $L_1$  and  $L_2$  lie gets into connection with the vapour branch. Hence on rise of temperature the three-phase line  $S + L_1 + L_2$  merges continuously into  $S + L_1 + G$ . Then the points  $L_2$  and  $G$  of the three-phase line  $S + L_2 + G$  which lie on the transverse plait at low temperature, are both found on the closed portion in the transformation; hence the three-phase line  $S + L_2 + G$  terminates in the hidden plaitpoint  $P_2$ , where the line for fluid by the side of solid touches the closed portion. Without our entering into any further particularities, it will be clear in my opinion, that fig. 4 indicates the  $P, T$ -projection holding for this case. That again a transition takes place by means of an unstable ridge, can be shown in perfectly analogous way as in the transition described in § 3.

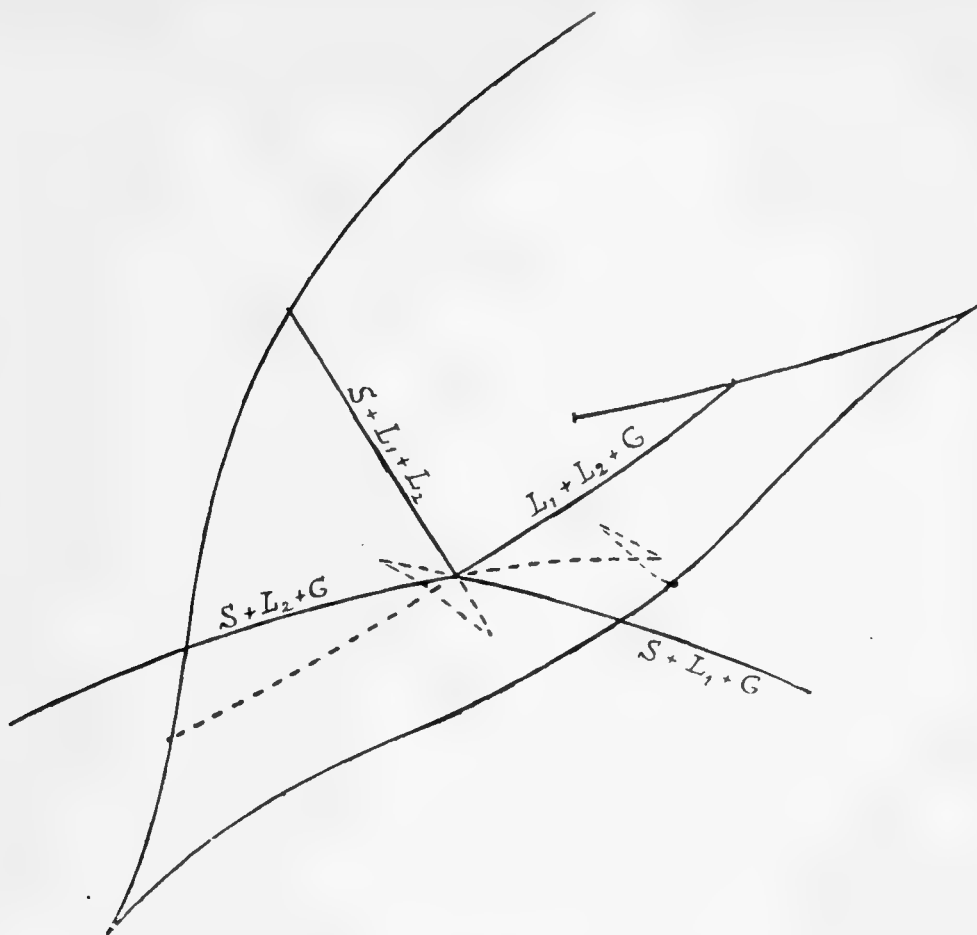


Fig. 4.

6. It will be clear that the number of cases possible compared with those of the first case of § 3 and § 4 will be smaller here, as only one of the components can appear as solid substance, but that on the other hand the transformation of the plait gives rise to a complication.

If we again take the case of § 5, the transformation can take place before the state  $g$  has been reached, as described above. If, however, the temperature of  $g$  is lower than that of the transformation, then just as before, the three-phase line  $S + L_1 + L_2$  continues to terminate in the hidden plaitpoint  $P_2$ , and so, though the shape of the critical line is entirely different from that in § 3, we have the same connection of the three-phase lines  $S + L_1 + G$  and  $S + L_2 + G$ , and two critical points on  $S + L_1 + L_2$  and  $L_1 + L_2 + G$ .

In analogy with § 4 we can also imagine that the longitudinal plait makes its appearance and is transformed after the solid-fluid line in the figure has been shifted some distance to the left, and then overtakes the solid-fluid line. In this case we shall again have to distinguish two cases, viz. that the transformation appears before or after the state  $g$ .

In the first case the three-phase line, which begins in the unstable

plaitpoint, will terminate in the critical point  $P_3$  of the transverse plait, which has detached itself from the side, and a stable critical end-point occurs with the properties described by SMITS in the system ether-anthraquinone. The three-phase line  $S + L_1 + G$  then merges continuously into the three-phase line  $S + L_1 + L_2$ . If, however, the transformation takes place after the state  $g$ , the three-phase line that has started from  $P_2$  will pass into  $S + L_1 + L_2$ , and terminate in the stable plaitpoint  $P_1$ . Then the three-phase lines  $S + L_1 + G$  and  $S + L_2 + G$  are continuously connected, and the latter ends again in a critical end-point on the closed transverse plait, which has detached itself.

Finally we should still take into account the possibility that the line for fluid can possess the shape of line  $p$  in fig. 1, and also for this case we get four types of quadruple points, which, however, differ only slightly from the preceding types.

All the possibilities, however, agree in this that either two critical points occur on the three-phase lines  $S + L_1 + L_2$  and  $L_1 + L_2 + G$ , and the continuous connection takes place between  $S + L_1 + G$  and  $S + L_2 + G$ , or one of the three-phase lines  $S + L + G$  is in connection with  $S + L_1 + L_2$ , and the other three-phase line  $S + L + G$  possesses one or two critical points.

7. In the preceding paragraphs we have pretty completely discussed the types which can possess quadruple points, in which the components occur as solid phases. The occurrence of mixed crystals and compounds does not give rise to essential modifications. All the same different types should be distinguished for these cases; this follows, namely, already from the fact that with the discussed quadruple points the solid substances always possess either the greatest or the smallest concentration, and so the possibility was excluded that the concentration of the solid substance lies between that of the coexisting liquid and vapour phases. To form an opinion of these cases the most rational way would be to have recourse to the  $\psi$ -surface; this alone can give a complete insight into the peculiarities that occur for a definite case. Generally, however, we can avoid this course; but then the danger is great to assume possibilities, which would appear to be physically impossible if the  $\psi$ -surface was consulted. To escape this danger, and to avoid on the other hand the more laborious way via the  $\psi$ -surface, I will here draw attention to a rule which gives a relation between the relative situation of the three-phase lines and the concentrations of the coexisting phases.



The simplest way to state this rule is in my opinion as follows.

*The region that does not possess metastable prolongations of three-phase lines in the  $P, T$ -projection is that of coexistences of phases of consecutive concentration.*

Perhaps the clearest way to set forth the meaning will be by means of fig. 2.

If we produce the four stable three-phase lines through the quadruple point, as has been done in fig. 2, it appears that no metastable prolongations occur in the region between  $S + L_1 + L_2$  and  $L_1 + L_2 + G$ . The region in question indicates the coexistence of  $S + L_1$ ,  $L_1 + L_2$  and  $L_2 + G$ . These coexistences refer every time to two phases consecutive in concentration, i. e. if the four phases are arranged according to their  $x$ -values, the succession is  $S L_1 L_2 G$ . That this is really the case in fig. 2, is clear since it

has been assumed there that  $\left(\frac{dp}{dx}\right)_v$  is positive, that by  $L_1$  the liquids were denoted which lie on the lefthand of the longitudinal plait, and that the first component appears as solid substance.

8. To prove the rule in question we will indicate the phases arranged according to their  $x$ -values in the quadruple point, by 1, 2, 3, and 4, so disregarding altogether what state of aggregation the phases possess. The four three-phase lines  $1 + 2 + 3$ ,  $1 + 2 + 4$ ,  $1 + 3 + 4$  and  $2 + 3 + 4$  divide the space round the quadruple point in the  $P, T$ -projection into four parts, which every time indicate pressures and temperatures of two-phase regions. We know besides that every three-phase line forms the boundary of three two-phase regions, and so that on one side of the three-phase line one, on the other side two regions occur, where every time a combination of two of the three phases are in equilibrium. In the first place it is now clear that none of the two-phase regions can have an angle at the quadruple point which is greater than  $180^\circ$ . If this were so we should be able to produce one of the bounding three-phase lines through the quadruple point. This metastable prolongation would then lie in the region where two of the three phases could coexist in a stable way; then, by the side of these two the third could also occur stable on the three-phase line, which is evidently impossible, because the prolongation represents metastable states.

Every quadruple point which contains a two-phase region with an angle that is larger than  $180^\circ$  is therefore impossible. If we take this into account, the thesis in question can be simply derived. For this purpose we first take the coexistence of the phases with the

extreme  $x$ -values, so 1 and 4, then the two-phase region  $1 + 4$  will occupy all the available width in the spacial figure; this region forms a space which has the full width of the four-phase line as boundary. So with the same pressure and temperature no other stable two-phase equilibrium is possible there. The two other two-phase equilibria  $1 + 2$  and  $2 + 4$ , which lie by the side of the three-phase line  $1 + 2 + 4$ , and the equilibria  $1 + 3$  and  $3 + 4$ , which lie by the side of the line  $1 + 3 + 4$ , lie therefore always on the other side of the lines in question in the  $P$ ,- $T$  projection.

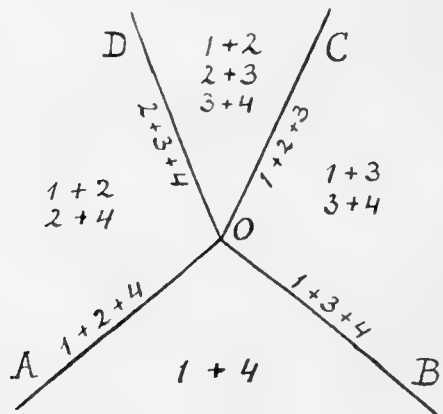


Fig. 5.

So in fig. 5 the situation of the region  $1 + 4$  determines that of the two three-phase lines  $AO$  and  $BO$ , and at the same time that of the regions  $1 + 2$ ,  $2 + 4$ ,  $1 + 3$ , and  $3 + 4$ . So it now remains to decide what the situation is of the two remaining three-phase lines. It is now easy to see that the line  $OC$  lying on the right must represent the coexistence of  $1 + 2 + 3$  and the line  $OD$  that of  $2 + 3 + 4$ . The line  $OC$ , namely, must bound on one side either the region  $1 + 3$  or the region  $3 + 4$ . This can only take place by the three-phase line  $1 + 2 + 3$ , because in the other case besides  $3 + 4$ , also the region  $2 + 3$  would have to lie on the same side of the three-phase line, which can evidently not be the case. So now, the situation of the phases is quite determined. So it appears that one two-phase equilibrium occurs in the region  $AOB$ , two in the regions  $BOC$  and  $DOA$ , and three in  $COD$ .

Now the angle  $AOB$  must contain the metastable prolongations of the two three-phase lines  $CO$  and  $DO$ . Suppose namely, that the prolongation of  $CO$  should fall in  $DOA$ , then the region  $1 + 2$  should present an angle which is greater than  $180^\circ$ ; if the prolongation of  $DO$  lay in  $COB$ , then the region  $3 + 4$  would possess an angle greater than  $180^\circ$ . So it has been proved that only such a situation is possible that no prolongation falls in the angle  $COD$ . And this proves the stated rule.

It will, moreover, be clear from the above proof, that the thesis might also be stated as follows:

If the phases, arranged according to their  $x$ -values, are expressed by 1, 2, 3, and 4, the angle without metastable prolongations lies between the three-phase lines  $1 + 2 + 3$  and  $2 + 3 + 4$ .

9. The application of this rule can naturally be twofold. At

certain values of the concentration it is easy to distinguish, what quadruple points can occur and what cannot. And in the second place it furnishes a simple means to read directly the consecutive order of the concentrations from the observations of the three-phase lines.

The former kind of applications is of course far more numerous than the second. There are, namely, only few cases as yet, in which the situations of all four three-phase lines at the quadruple point are determined.

To elucidate the former kind of applications, I will briefly examine what the rule requires for some known quadruple points. The quadruple point of the ordinary spacial figure, in which the succession of the phases is  $S_1 G L S_2$ , has to fulfil the demand that the region between  $S_1 + G + L$  and  $G + L + S_2$  does not contain metastable prolongations.

If we consider the quadruple point of two salt-hydrates by the side of liquid and vapour, in which the order of the concentrations is  $G L H_1 H_2$ , the rule in question demands that no metastable prolongations occur between the three-phase lines  $G + L + H_1$  and  $L + H_1 + H_2$ . This rule both holds for the ordinary case that the hydrate  $H_1$  rich in water is transformed into that which is poor in water on rise of temperature and for the "inverse melting-points", where the reverse takes place. For the former case the rule requires among others that the prolongation of  $H_1 L G$  lies at lower pressure than the stable part of  $H_2 L G$ , and reversely, which must really be the case, as is known.

What type of quadruple points must be expected in the case of an "inverse melting-point", will be discussed a little more fully here.

If we think the transformation of the two salt-hydrates to take place in such a way that the one rich in water exists at higher temperature than that poor in water, then the quadruple point will have to satisfy besides the above-mentioned demand, also the condition, that at temperatures below the quadruple point the three-phase line  $G + L + H_2$ , above it the line  $G + L + H_1$  is stable. If we further consider that on the three-phase line  $L + H_1 + H_2$  the transformation  $H_2 + L \rightarrow H_1$  occurs on isobaric supply of heat, and this will probably be accompanied with volume-contraction; that on the three-phase line  $G + H_1 + H_2$  the transformation  $H_2 + G \rightarrow H_1$  occurs on supply of heat, and that this is certainly accompanied with volume-contraction, then we know that probably both, but certainly the line  $G + H_1 + H_2$  possesses a negative value for  $\frac{dp}{dT}$ .

If we take this into account for both lines, then it will be clear that this quadruple point will present the shape of fig. 6, where the angle between  $L + H_1 + H_2$  and  $G + L + H_1$  does not contain metastable prolongations. I shall postpone a discussion of the further peculiarities which appear for inverse melting-points, to a later occasion.<sup>1)</sup>

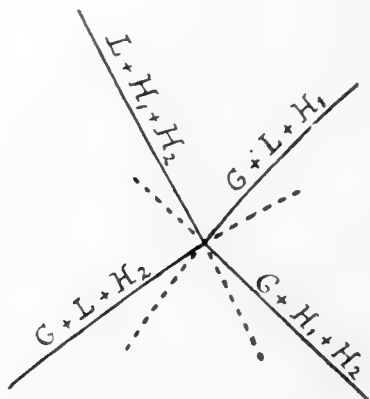


Fig. 6.

Another example, in which the rule enables us to infer easily what quadruple points are possible, we find among others for a dissociating compound in solid state by the side of the least volatile component, liquid and vapour; then we know that this quadruple point can occur on different branches of the three-phase line: compound + liquid + vapour.

Let us consider the case that the pressure continually decreases from the first to the second component; then the quadruple point can lie in the first place on the three-phase line so that neither melting-point, nor maximum sublimation point appear stable. If this is the case then the order of the phases is  $G L V S$ , in which  $V$  denotes the solid compound,  $S$  the solid second component. The angle without metastable prolongations lies therefore between  $G + L + V$  and  $L + V + S$ , and in this the coexistences  $G + L$ ,  $L + V$  and  $V + S$  occur according to the first formulation of the rule.

If, however, on the three-phase line of the compound the melting-point occurs, but the maximum sublimation point does not occur, the succession has become  $G V L S$ , so that just as in the preceding case we cannot meet with metastable prolongations in the angle between  $G + V + L$  and  $V + L + S$ , and now find the coexistences  $G + V$ ,  $V + L$  and  $L + S$  between the two lines. As is known this case is found among others when a salt-hydrate (before its transition to the anhydrous salt or to another hydrate) possesses a melting point.

If the compound has both a melting-point and a maximum point of sublimation, the order has become  $V G L S$ , and no metastable prolongation occurs in the angle between  $V + G + L$  and  $G + L + S$ , where the coexistences  $V + G$ ,  $G + L$ , and  $L + S$  are found.

Led by these considerations we can easily construct the quadruple points under discussion.

<sup>1)</sup> A similar type of quadruple points we find also in the system Iron-carbon. SMITS. Z. f. Elektrochemie 18. 362 (1912).

In conclusion one of the few applications of the second kind may be briefly mentioned here.

In my first communication<sup>1)</sup> concerning the system hydrogen sulphide-water I have fully determined the situation of the quadruple point S (hydrate) by the side of two liquids ( $L_1$  and  $L_2$ ) and gas (G) with the three-phase lines terminating there. If this rule had been known to me already then, I could have directly inferred from the figure of the cited communication that between the three-phase lines  $S + L_1 + G$  and  $S + L_1 + L_2$  no metastable prolongations occur, that there the coexistences:

$S + L_1$  (angle  $< 180^\circ$  between  $S + L_1 + G$  and  $S + L_1 + L_2$ )  
 $L_1 + G$  „ „ „  $S + L_1 + G$  and  $L_1 + L_2 + G$ ) and  
 $S + L_2$  „ „ „  $S + L_2 + G$  and  $S + L_1 + L_2$ )

occur, and that therefore the order of the phases must be  $GL_1SL_2$ , if the mentioned coexistences are to take place between phases that are consecutive in concentration. The gas of these phases containing the greatest quantity of hydrogen sulphide, it is clear that the hydrate contains less water than  $L_2$ , and that therefore the liquid  $L_2$  lies on the side of the water. From determinations which I carried out later on, and which I have communicated in my second paper<sup>2)</sup> on this system it appears that this conclusion is really valid.

*Anorganic Chemical Laboratory of the University.*

*Amsterdam, September 18, 1912.*

**Physics.** — “*Isotherms of diatomic substances and of their binary mixtures. XII. The compressibility of hydrogen vapour at, and below, the boiling point.*” By H. KAMERLINGH ONNES and W. J. DE HAAS. Communication N<sup>o</sup>. 127c from the Physical Laboratory at Leiden.

(Communicated in the meetings of May 25 and June 29, 1912).

§ 1. *Introduction.* To the region covered by the investigations which have been made for many years past in the Leiden laboratory upon the equation of state for hydrogen at low temperatures (for the latest paper see Comm. N<sup>o</sup>. 100a, Proc. Dec. 1907) the present Communication adds the region for hydrogen vapour lying between  $-252^\circ$  C. and  $-258^\circ$  C. While the lowest reduced temperature

<sup>1)</sup> These Proc. January, 1911. p. 829.

<sup>2)</sup> These Proc. June, 1911. p. 195.

attained in the measurements of KAMERLINGH ONNES and BRAAK was about  $t = 2.2$ , in our present investigation we were able to calculate the second virial coefficient  $B$  for the further region from  $t = 0.7$  to about  $t = 0.5$ ; by this means, since interpolation between  $t = 0.7$  and  $t = 2.2$  is not a matter of any difficulty,  $B$  becomes known over a very extensive region of reduced temperature (from  $t = 0.5$  to  $t > 12$ ). The second reduced virial coefficient is therefore known for a single substance over a much more extensive region of temperature than has hitherto ever been the case. This extension was especially to be desired as, in the first place, it allows a better comparison from the point of view of the law of corresponding states of  $B$  for hydrogen with its value for various other substances, and this will become of particular importance when the comparison can be extended so as to embrace monatomic substances (a communication by KAMERLINGH ONNES and CROMMELIN will shortly appear dealing with the  $B$  for argon at low reduced temperatures). In the second place it allows us to put to the test theoretical deductions concerning  $B$  (for instance, the connection between the peculiarities of  $B$  with the peculiarities of the specific heats and of viscosity, and also of the dielectric constants and of penetrability by electrons). This is all the more important as  $B$  is related to that state which according to REINGANUM can be called the *planetary* gas state in which, in allowing for the influence of collisions between molecules, only two molecules need be considered, as the possibility of the proximity of others may be neglected.

From  $B$ , moreover, one can calculate the experimentally determined corrections of the hydrogen thermometer scale to the AVOGADRO-scale, which have hitherto been known only down to  $-217^{\circ}$  C., down to the lowest temperatures which can be measured with the hydrogen thermometer. (Cf. Comms. Nos. 101*b* and 102*b*).

The uncertainty in the adjustment of a cryostat bath to an accurate definite temperature and in the measurement of that temperature is much greater than that with which a temperature, once steadied, can be maintained constant. Since, now, uncertainty in the determination of the temperature is of great influence upon the values of  $B$  obtained from the observed  $pv_A$ , it was decided to proceed with isothermal measurements so as to be as independent as possible of thermometrical measurements. A further advantage of constancy of temperature in the comparison of values of  $pv_A$  at different pressures lies in the circumstance that the possible difference between the temperature of the gas in the piezometer and that of the thermometer in the bath is constant throughout. The advantages of isothermal measure-

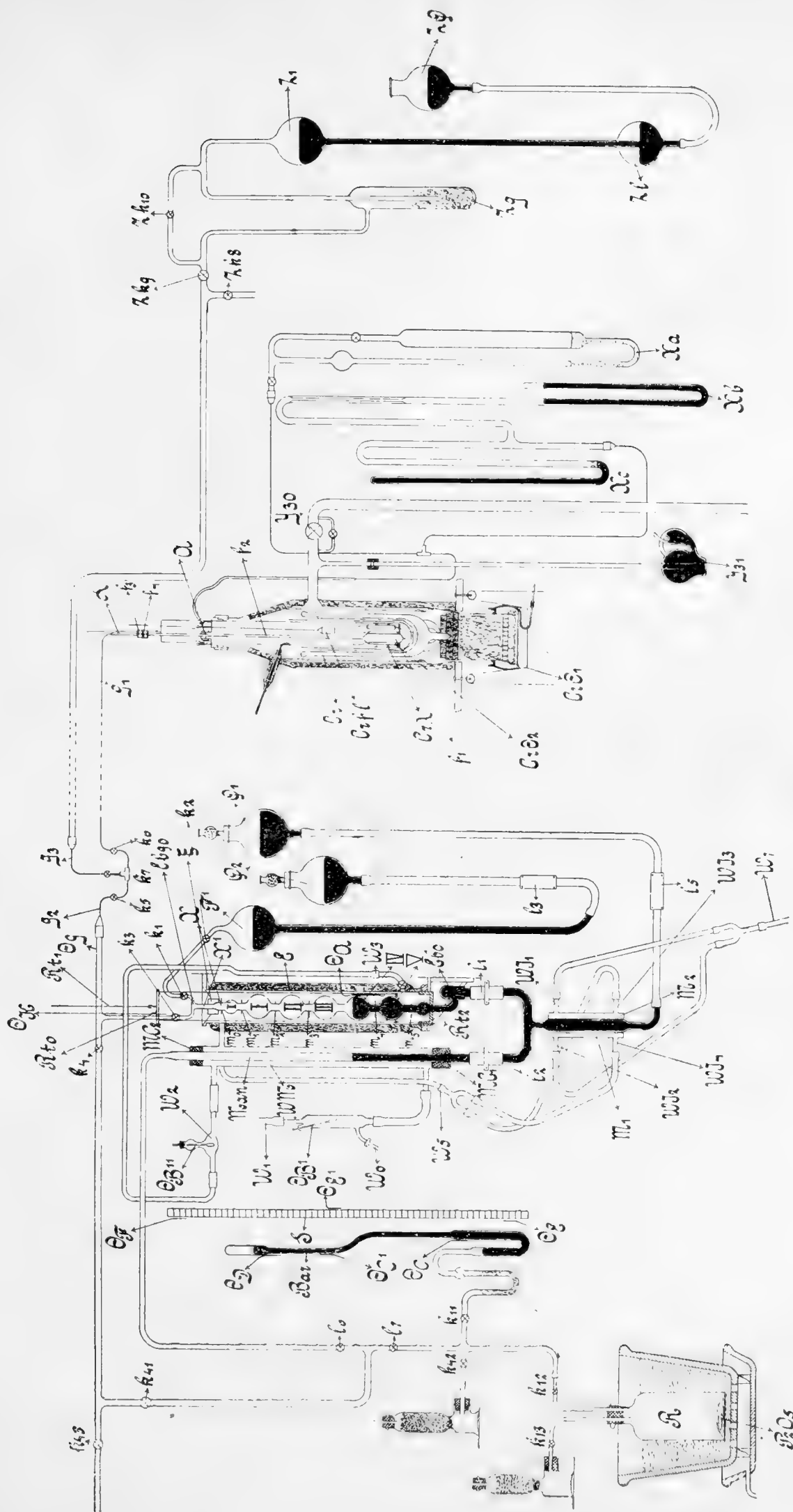


Fig. 1.

ments would have been far greater for us had we not frequently been obliged to aim at obtaining the same reading of the resistance thermometer instead of at the maintenance of a definite temperature.

The investigation was carried out at three temperatures, approximately  $-252^{\circ}.6$  C.,  $-255^{\circ}.5$  C. and  $-257^{\circ}.3$  C. A lower temperature than  $-257^{\circ}.3$  was not desirable as the smallest pressure to be measured at this temperature had already sunk as low as 5 cm. and further progress in this direction would have necessitated another apparatus.

For each isotherm the densities were so chosen that the ratio of the extreme densities was about two to one in each case. By this means it was brought about that in the solution of  $B_A$  from the two equations

$$\begin{aligned}pv_{A_1} &= A_A + B_A d_{A_1} + C_A d_{A_1}^2 \\pv_{A_2} &= A_A + B_A d_{A_2} + C_A d_{A_2}^2\end{aligned}$$

the coefficient of  $B_A$  was approximately 1. In this solution  $C_A$  was taken as a correction term from the equation of state VII. H<sub>2</sub>.3 (formula (16) Comm. N<sup>o</sup>. 109a).

Finally, for practical reasons, it was necessary to remain as far as possible away from the region of condensation, as a sudden fluctuation of the temperature could quite well occasion condensation to take place upon the walls of the piezometer, and particularly of the capillary, and this, in view of the excessively slow liberation of liquid and vapour from the glass, would render the measurements valueless.

The measurements were made with a piezometer immersed in a bath of liquid hydrogen and connected through a capillary with the volumenometer studied in detail in Comm. N<sup>o</sup>. 127a (See Fig. 1, p. 407). The piezometer was first evacuated and a quantity of gas measured in the volumenometer; the valve between the two was then opened. Pressure equilibrium was then allowed to establish itself at the desired value, and then the pressure and the quantity of gas remaining in the volumenometer were determined.

## § 2. *Arrangement of experiments. Auxiliary apparatus.*

The experimental arrangements are shown in fig. 1, p. 407<sup>1)</sup>. One portion of the apparatus had already been utilised in the investigation of the diameter for oxygen, and is described in Comm. N<sup>o</sup>. 117, Proc. Febr. 1911. The left hand part of fig. 1, p. 407 is an impro-

<sup>1)</sup> In the drawing some details of no importance are incorrectly represented, viz: the ice ought to cover the bottle *R*, the air-trap *Zl* is in reality much smaller, the safety-tube *Y*<sub>3</sub> is of course not wholly filled with mercury.



ved copy of the left hand part of Pl. I of that Communication, to which we may in the first place refer. The improved diagram embraces the modifications which were introduced later, and which are described in Comm. No. 121*a*. Identical parts are indicated by the same letters in fig. 1 and in Comms. Nos. 117 and 121*a*, parts which have undergone modification are distinguished by accents, while parts which are new or are now lettered for the first time have new letters attached to them. We may refer to W. J. DE HAAS'S thesis for further details concerning the water circulation,  $W$ , which, supplied from the thermostat, keeps constant and uniform the temperature of the volumenometer and of the manometer.

The volumenometer is connected to the auxiliary reservoir  $F'$  through the taps  $k_1$  and  $k_2$ . This allows one to add gas to the measured quantity contained in the volumenometer, or to temporarily abstract a measured quantity from the volumenometer. This was essential in our experiments as the volume of the piezometer, in which the gas density was sometimes practically 20 times as great as that in the volumenometer, was 110 c.c. and that of the volumenometer was not more than 1250 c.c. Hence, if, for instance, the volume is adjusted to the smallest volume in the volumenometer (the neck  $m_0$  in the figure) at a pressure of one atmosphere, then even when the volumenometer is completely filled (to the neck  $m_5$  in the figure) the second equilibrium pressure of half an atmosphere, which, according to § 1, is desirable in this case, is not yet attained. The admission of gas from the volumenometer to  $F'$  and vice versa can be of use in another way, viz. in the transition to another temperature and in the adjustment of pressure equilibrium. In the course of our experiments, however, we have not been able to make such free use of the auxiliary reservoir as we should have liked. The volumenometer can be evacuated through the valves  $k_3, k_4, k_{43}$ ; and it can be connected to the barometer and to the constant pressure reservoir,  $R$ , (Comm. No. 60, Pl. VI) through  $k_3, k_4, k_{41}, l_7, k_{11}, k_{12}$ . When the volumenometer adjustments and the value of the pressure permit of it, the valve  $l_7$  may be closed and the pressure then determined from the manometer  $M$  alone, the space above which is then evacuated through  $l_6$ . We may refer to Comm. No. 121*a* by W. J. DE HAAS for further details concerning the pressure measurement.

To ascertain when pressure equilibrium has been attained we applied the method already described in Comm. No. 127*a*; the pressure in the volumenometer was under constant observation, and from the curve expressing the pressure as a function of the time, we deduced, during the observations, the time at which the pressure difference

originally existing between the volumenometer and the piezometer had sunk to a value that was insignificant. The reliability of this method is shown by the calculations published by W. J. DE HAAS in Comm. No. 127*a*. For assistance rendered in the application of this method and for further help given in the course of this research we should like to express our indebtedness to MRS. DE HAAS-LORENTZ.

Readings were taken with a very fine Société Genevoise cathetometer with three telescopes<sup>1)</sup>, each with a micrometer eyepiece and level. A scale with very accurate subdivisions (Comm. N<sup>o</sup>. 60) was used for the readings with the micrometer eyepieces.

Communication between the volumenometer and the piezometer (see the right hand portion of the diagram) was obtained through the tap  $k_3$ , the glass *T*-piece (closed on the other side by  $k_4$ ) over which a connecting tube is cemented, a copper capillary  $g_2$  (to give a certain elasticity to the connections), the steel taps  $k_5, k_6$ , a steel capillary  $g_1$  and a glass capillary  $f_2$ . The steel taps  $k_5, k_6, k_7$ , were provided with selected cork packing and were kept for about half an hour at a pressure of 50 atm. They closed perfectly. Connections between steel and glass capillaries were also made with the greatest care. This connection was made by means of a brass screw soldered to the glass capillary, the capillary being very slightly rounded and projecting about  $\frac{1}{4}$  mm. beyond the screw; this joint sustained a high vacuum for a long time. The rounded end of the glass capillary was covered with a packing ring made of fibrous plate, and could be screwed with force into the brass nut soldered to the steel capillary.

The diagram does not show the wool with which all the principal parts of the apparatus were wrapped. The barometer was wrapped with the greatest care in wool, and was, moreover, surrounded by a double layer of paper so as to eliminate all convection currents.

<sup>1)</sup> Compare the similar adjustments of Comm. No. 95*e*, Table I.

The difference between the levels of the top and the edge of the meniscus and between the top of the meniscus in one of the necks and the central line on a screen (Cf. Comm. No. 84, Pl. II, Proc. March 1903) can be obtained with sufficient accuracy and more quickly from the cathetometer scale than with the standard scale and level and the micrometer eyepiece. In the majority of cases it is sufficient and much simpler still to estimate these differences of level from the standard scale without focussing the micrometer upon the divisions of the standard scale at all. For an error of 10% in the determination of the height of the meniscus leads to an error of 1% in the capillary depression; and an error of 1 mm. in the estimation of the height of a line on the screen induces an error of only 16 or 17 mm<sup>3</sup>. in the volume, which makes a difference of only 1 in 60,000 in the volume of gas usually employed.

Neither are the numerous thermometers shown in the diagram which were suspended along the whole apparatus.

Finally, the connections  $Zk_9$ ,  $Zk_{10}$  lead to the hydrogen reservoir  $Z_1$ . To this reservoir is attached a side tube with a valve,  $Zk_8$ , through which the whole apparatus can be filled with hydrogen; it is also provided with a purifying chamber  $Zg$ , through which the gas passes on its way to the measuring apparatus and consisting of a tube filled with glass wool surrounded by a DEWAR flask containing liquid air. After the measurements the gas can be collected in  $Z_1$  through  $Zk_9$ ,  $Zk_{10}$ .

We may refer to Comms. Nos. 83, 94c, 94d, 94e, and 121a for descriptions of the thermostat, the water circulation and the cryogenic bath and auxiliary apparatus.

§ 3. *The hydrogen.* The apparatus was filled with distilled hydrogen by means of the arrangement described in Comm. N°. 94e, § 2; the tap  $Zk_9$  (see fig. 1) was utilised for the repeated evacuations and washings with hydrogen.

§ 4. *The temperatures.* The thermostat supplied the water circulation,  $W$ , with water at very uniform temperature. (See Comm. N°. 121a).

Stirring was continuous during the measurements. A thermometer divided into 20-ths of a degree and calibrated by the Reichsanstalt was attached to the stirrer of the volumenometer, the mean temperature being thus obtained. The influence was studied beforehand of fluctuations in the room temperature upon that of the water in the jacket surrounding the volumenometer, and it was found sufficient to keep it constant to within one deg. Cent. This was always done. (For further details see dissertation by W. J. DE HAAS). Every determination of the volumenometer temperature can then be regarded as certain to within  $0^{\circ}.02$  C.

The temperature of the cryostat was regulated in the usual way; great care was devoted to keeping it constant by Mr. G. HOLST, whom we wish to thank for his assistance. It would take up too much space here to give all the curves of this temperature regulation, but as an example we may state that in the determination of the isotherm at  $-255^{\circ}.5$  C., made on the 24<sup>th</sup> of June, and on the 8<sup>th</sup> and 14<sup>th</sup> of July, 1911, the values of the differences at five points from the first determination were

0.005,      0.012,      0.010,      0.000 degrees Centigrade.

This corresponds to an uncertainty of 0.00004 in the value of  $pv_A$ .

The temperature of the bath was furnished by the determinations themselves. See § 6.

§ 5. *Calibration, Constants and calculation of corrections.*

*a. Pressures.*

The corrections, and in particular the optical corrections, for the apparatus have already been discussed in part in Comm. N<sup>o</sup>. 121*a*.

The pressures were always reduced to the normal atmosphere of 45° N. For this the value of the Leiden atmosphere, 75.9463<sup>1)</sup>, was used. The following corrections were applied to the pressures:

1. A temperature correction for the inequality between the temperatures of the mercury in the manometer and in the volumenometer (Comm. N<sup>o</sup>. 121*a*).

2. A correction for the standard meter which is 999.91 mm. at 0° C. (Comm. N<sup>o</sup>. 70).

3. An optical correction for the refraction of light by the glass windows (Comm. N<sup>o</sup>. 121*a*) and by the manometer tube.

4. A correction for the capillary depression. These corrections were tabulated for various widths of tube, being obtained from KELVIN'S graphical construction and from LOHNSTEIN'S<sup>2)</sup> formula.

5. A correction for KNUDSEN'S transpiration pressure<sup>3)</sup>.

6. A correction, where necessary, for the pressure of the air column between the lower barometer meniscus and the manometer meniscus.

7. A correction for the aerostatical difference between the pressure in the volumenometer and that in the piezometer was neglected.

A discussion of the degree of accuracy attained in the determination of the pressure has already been given in Comm. N<sup>o</sup>. 121*a*.

*b. Volumes.*

Reference may be made to Comm. N<sup>o</sup>. 121*a* for the calibration of the volumenometer.

The volumes as measured were always corrected at their calibration temperature. This correction was always very small.

A correction for the compression of the glass vessels was applied by means of the formula

$$\frac{\delta V}{V} = \frac{3}{2} \frac{(1-\mu)(p_i - p_e)}{E} \frac{R}{d}$$

<sup>1)</sup> This value has been calculated with the number for the gravity at Leiden used in Comm. N<sup>o</sup>. 60, Sept. 1900, p. 304, and  $g_{\text{norm}} = 981.625$  according to Suppl. N<sup>o</sup>. 23, "Einheiten" *a*. (Note added in the translation).

<sup>2)</sup> F. LOHNSTEIN. Ann. der Physik (4) 33 (1910), n<sup>o</sup>. 2.

<sup>3)</sup> M. KNUDSEN. Ann. der Physik (4) 31 (1910), n<sup>o</sup>. 3.

in which  $E = 6500$  K.G./mm<sup>2</sup>.,  $\mu = 1/4$ ,  $R = 3.9$  cm.,  $d = 0.5$  mm. (See Comm. N<sup>o</sup>. 88).

In the calculation of the volumes, the volumes of the mercury menisci were taken from the table given by SCHEEL and HEUSE<sup>1)</sup>.

As regards the accuracy of the volumes measured we may remark that a variation of one degree in the temperature causes a change of only 1 in 40000 in the volume. The correction for the compression gives  $\frac{1.3}{10000}$  for  $\frac{\delta V}{V}$  at the lowest pressure measured (5 cm.). If this correction is applied, the remaining uncertainty is certainly less than  $1/10000$ .

As regards the volume of the mercury menisci as, for instance, in the case of  $2R = 14.8$  mm. where the volume is 179.4 mm<sup>3</sup> for a meniscus height of 1.6 mm., and 192.2 mm<sup>3</sup> for a height of 1.7 mm., the error for heights lying between these two values is certainly not so great as 10 mm<sup>3</sup>. This is certainly negligible in a volume which would, at ordinary temperature, be at least 1200 cm<sup>3</sup>. seeing that the volume of the piezometer is 110 cm<sup>3</sup>. and contains gas of density from 12 to 20 times the normal. The same may be said of the uncertainty in the volume of the dead space. Such portions of this as were not separately calibrated with mercury (steel and glass capillary, see dissertation DE HAAS) were volumetrically calibrated. The total dead space was about 10 cm<sup>3</sup>. An error of 1 % in the calibration or of 3 degrees in the temperature causes an uncertainty of 100 mm<sup>3</sup>. This is only 1 in 12000 of the 1200 cm<sup>3</sup>. just mentioned. The volume calibration, however, was much more accurate, while, as was stated above, the room temperature was kept constant to within a degree.

These comments are also all applicable to the determinations of Comm. N<sup>o</sup>. 121a.

The accuracy attained in the calibration of the piezometer was greater than 1 in 10000 (cf. dissertation DE HAAS). The volume was corrected for the temperature of the cryostat by means of the formula

$$v_t = v_0 \left[ 1 + \left\{ k_1 \frac{t}{100} + k_2 \left( \frac{t}{100} \right)^2 \right\} 10^{-6} \right]$$

in which

$$k_1 = 2343$$

$$k_2 = 272$$

(See Comm. N<sup>o</sup>. 95b, § 1). The error arising from this method can only be very small.

Temperature corrections for the gas in the glass capillary were

<sup>1)</sup> K. SCHEEL and W. HEUSE. Ann. d. Phys. (4) 33 (1910), n<sup>o</sup>. 2

applied in the manner published in Comm. N<sup>o</sup>. 97*a* § 8: For this, the temperature distribution along the stem was taken from Comm. N<sup>o</sup>. 95*e*. That this temperature distribution is approximately correct was apparent, moreover, from the time it took pressure equilibrium to be established. Cf. Comm. N<sup>o</sup>. 127*a*.

Collecting all these, we may regard the volumes occupied by the cooled gas as certain to within 1 in 10000. Allowing for what we have already stated regarding the pressure, but not taking temperature uncertainty into account, we may expect an accuracy of 0,00002 in the  $pv_A$ 's, or, at the highest pressure to within one fivethousandth, and at the lowest pressure, to within  $1/_{2500}$ <sup>th</sup> of the value of  $pv_A$ .

§ 6. *Calculation and Results.* The quantities of gas were always expressed in terms of the normal volume. For this purpose equation I of Comm. N<sup>o</sup>. 127*a* was used:

$$pv_{A20^{\circ}C} = 1.07258 + 0.000667 d_{A20^{\circ}C}.$$

Using, where necessary, an approximate temperature as a correction factor for the piezometer, the measurements yielded values of  $d_A$ , the density of the gas in the piezometer under the observed pressure. The temperature of the gas in the piezometer for each series was obtained from the  $pv_A$  itself for that particular series. For that purpose values of  $C_A$  in

$$pv_A = A_A + B_A d_A + C_A d_A^2$$

were used in the calculation which were obtained for each (at first approximate) temperature from the special reduced equation of state for hydrogen VII. H<sub>2</sub>. 3 given in Comm. N<sup>o</sup>. 109*a* equation (16) which was deduced from the observations of KAMERLINGH ONNES and BRAAK and adjusted to a temperature of  $-217^{\circ}C$ .  $A_A$  and  $B_A$  then follow from our observations and also  $pv_A$  at the same temperature for the density of the gas in the hydrogen thermometer of 1100 mm. zero pressure. From this with

$$(pv_A)_{ts} = (pv_A)_0 (1 - 0.0036627 t_s)$$

we finally obtain the temperature on our hydrogen thermometer of 1100 mm. zero pressure.

The temperatures obtained in this way yield a calibration on the hydrogen scale of the resistance thermometer whose readings serve as a guide to the regulation of the temperature of the bath. This resistance thermometer was also calibrated with the hydrogen thermometer independently. The two calibrations are not quite in agreement. A subsequent paper by KAMERLINGH ONNES and HOLST will return to the question of this difference.

We obtained (where  $t_s$  is the temperature on our hydrogen thermometer of zero pressure 1100 mm.):

TABLE I. H<sub>2</sub>. Values of  $pv_A$ .

Series	No.	$t_s$	$p$	$d_A$	$pv_A$	O—C
I. 23 and 29 June 1911	1	} — 252°.63	0.34786	4.7568	0.073129	
	2		0.60358	8.4597	0.071348	
II. 24 June 8 and 14 July 1911	1	} — 255°.46	0.10964	1.6918	0.064216	
	2		0.20672	3.2560	0.063469	0.000031
	3		0.27759	4.4133	0.062898	0.000012
	4		0.31318	5.0026	0.062603	0.000008
	5		0.31294	4.9992	0.062598	
III. 14 and 18 July 1911	1	} — 257°.26	0.06698	1.1582	0.507834	
	2		0.13153	2.3031	0.057104	

The second series was represented by

$$pv_A = 0,065043 - 0,00489 d_A + C_A d_A^2$$

deduced from Nos. 1 and 5, with  $C_A$  as before, and the column O—C gives the differences between observation and calculation. These differences are smaller than those corresponding to the observed temperature fluctuations of the bath (see § 4), which is in agreement with the assumption that it is the mean temperature of the bath which must be taken as the temperature of the gas in the piezometer. This series also supports the use of the assumed  $C_A$ . Series I and III, lacking the controls possessed by series II in itself, are less reliable. Various circumstances have obliged us to postpone our

TABLE II.  
H<sub>2</sub>. Individual virial coefficients  $B_A$   
for hydrogen vapour

$t_s$	$B_{At}$
— 252°.63	0.000481
— 255°.46	0.000489
— 257°.26	0.000638

experiments for some time to come, so that for the temperatures of series I and III we have not been able to give such extensive series of measurements as in series II.

From Table I we finally obtain Table II (see p. 415)

§ 7. *Smoothed values of the virial coefficients, and corrections of the international hydrogen thermometer to the absolute scale.*

These corrections are to be determined from the virial coefficients  $B_A$  by the method employed by KAMERLINGH ONNES and BRAAK in Comm. N<sup>o</sup>. 101*b*. For this, however, it is desirable to use smoothed values. This was tried by plotting  $\log B$  as a function of  $\log T$ . Taking account of the accuracy of the various measurements there seemed to be much to recommend the smoothing given in Table III (in which the temperatures  $\theta = T - 273.09$  are given in KELVIN degrees, Table IV having been used for the calculation).

$\theta$	$B_{AT}$
— 252°.47	— 0.00047
— 255°.32	— 0.00049
— 257°.10	— 0.00055

In Table IV these values of  $B_{AT}$  have been used to supplement by data for — 252° C., — 255° C. and — 257° C. the list given in Comm. N<sup>o</sup>. 101*b* of experimental corrections  $\Delta t_i = \theta - t_i$  of the international hydrogen thermometer to the absolute scale.

$t_i$	$\Delta t_i$ in degrees K.
— 252°.59 C.	+ 0.118
— 255°.45	+ 0.125
— 257°.24	+ 0.144



**Physics.** — “*On the second virial coefficient for di-atomic gases*”.

By Dr. W. H. KEESOM. Supplement N°. 25 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

§ 1. *Introduction. Synopsis of the more important results.* In Supplements N°. 24*a* (§ 1) and *b* (§ 6), in which the second virial coefficient was deduced from different particular assumptions concerning the structure and action of the molecule, a comparison was contemplated between the results then obtained and such experimental data as are at present available. The present paper will discuss some results obtained by carrying out such a comparison in the case of di-atomic gases. The importance of such a comparison, as well as of a comparison of the second virial coefficients for various gases, especially for di- and mon-atomic gases, from the point of view of the law of corresponding states, was emphasized in Comm. N°. 127*c*, § 1 (these Proceedings p. 405). That such a comparison can now be made with any fruitful result is due to the extensive series of accurate isotherm determinations made by KAMERLINGH ONNES and his collaborators, BRAAK, CROMMELIN, and W. J. DE HAAS.

In the present investigation a beginning is made with the di-atomic gases, especially with hydrogen, for these reasons: In the first place the most immediately indicated simplified hypothesis that can be made concerning the genesis of molecular attraction and can give any hope of agreement with experimental results<sup>1)</sup> is that first introduced by REINGANUM, which represents it as originating in the mutual electrostatic action of doublets of constant moment immovably attached to the molecules at their centres; this, together with the assumption that the molecules collide as if they were rigid spheres of central symmetry, leads to a value of the specific heat which agrees most closely with that of the di-atomic gases dissociating with difficulty at ordinary temperature; for these gases a law of dependence of  $B$  upon the temperature quite definite, and therefore ready to be tested, was deduced in Suppl. N°. 24*b* § 6 from the above assumptions. In the second place, values of  $B$  for hydrogen are known over a much more extensive temperature range than for any other gas with the

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<sup>1)</sup> See M. REINGANUM, Ann. d. Phys. (4) 38 (1912), p. 649 for the rejection of the explanation of molecular attraction by gravitation, or (at least of the total molecular attraction, cf. p. 429 note 2) by the magnetic action of series of magnetons assumed to be present in the molecules of paramagnetic and ferromagnetic substances.

exception of helium, but for helium values of  $B$  for temperatures below the BOYLE point are still comparatively uncertain.

The most important results yielded by the present investigation can be summarised as follows. The experimental results concerning the second virial coefficient for hydrogen above  $-100^\circ$  C. (the observations reaching  $+100^\circ$  C.) are consistent with the above assumptions of Suppl. N<sup>o</sup>. 24b § 6 (rigid spheres with constant doublets). Below  $-100^\circ$  C. hydrogen exhibits deviations from this behaviour which finally become considerable. Below the BOYLE point (the corresponding region of observation is from  $-180^\circ$  C. to  $-230^\circ$  C. for H<sub>2</sub>) hydrogen is found to correspond with argon, and also with helium in so far as the experimental data for helium at present available allow of any definite conclusion. It appears therefore that between  $-100^\circ$  C. and  $-230^\circ$  C., as far as  $B$  is concerned *the thermal behaviour of hydrogen also approaches that of a monatomic substance and eventually becomes the same*, as was found by EUCKEN<sup>1)</sup> to be the case with its caloric behaviour. This conclusion is supported by the results for the coefficient of viscosity.

It was also found that, as far as the second virial coefficient is concerned, the thermal behaviour of oxygen between  $0^\circ$  and  $200^\circ$  C., as deduced from AMAGAT's observations<sup>2)</sup> corresponds with that of a system of rigid spheres of central symmetry, each with a doublet of constant moment at its centre.

For nitrogen, on the other hand, within the same temperature region ( $0^\circ$  to  $200^\circ$  C., AMAGAT's observations) important deviations were found from the behaviour of rigid spheres of central structure each with an electric doublet of constant moment at its centre. With nitrogen in that temperature region, the dependence of  $B$  upon the temperature corresponds to that deduced from the assumption that the VAN DER WAALS quantities  $a_W$  and  $b_W$  are constant (Suppl. N<sup>o</sup>. 24a § 3); but then, however, the values given by BESTELMEYER and VALENTINER for  $B$  from  $81^\circ$  to  $85^\circ$  K. differ greatly from this.

§ 2. *Method.* Logarithmic diagrams were employed for the comparison of the experimental values of  $B$  with those deduced in Suppl. N<sup>o</sup>. 24 from various assumptions (cf. Suppl. N<sup>o</sup>. 23, Math. Enc. V 10, Nr. 33a). For this purpose  $\log B_N$  was plotted as a function of  $\log T$  upon transparent squared paper to a scale of 1 mm. = 0,005. Here, following Suppl. N<sup>o</sup>. 23,  $B_N$  represents the

<sup>1)</sup> A. EUCKEN. Berlin Sitz.-Ber., Febr. 1912, p. 141.

<sup>2)</sup> Cf. p. 428 note 1.

second virial coefficient when the empirical equation of state is written in the form :

$$pv_N = A_N \left\{ 1 + \frac{B_N}{v_N} + \frac{C_N}{v_N^2} + \frac{D_N}{v_N^3} + \frac{E_N}{v_N^4} + \frac{F_N}{v_N^5} \right\}, \quad \dots \quad (1)$$

while the subscript  $N$  indicates that the volume is expressed in terms of the normal volume as unit (cf. Suppl. N<sup>o</sup>. 23, Chapter on "Units"). Values of  $B_N$  were taken from the corresponding individual values of  $B_A$  which were given in previous communications by KAMERLINGH ONNES, and by him in collaboration with BRAAK, with CROMMELIN, and with W. J. DE HAAS. As we must remember that the latter coefficients  $B_A$ , belong to the empirical equation when written in the form of equation (II) of Comm. N<sup>o</sup>. 71 (June '01), and that the subscript  $A$  has there a meaning quite different from that attached to it in Suppl. N<sup>o</sup>. 23, they will be in the sequel distinguished as  $A_{(71)}$ . The reduction is then made by means of the relationship

$$B_N = \frac{B_{A(71)}}{A_{A(71)}} \dots \dots \dots (2)$$

It was first examined for each of the different gases if the temperature variation of  $B$  is in agreement with that deduced on the assumption of rigid molecules (cf. Suppl. N<sup>o</sup>. 24a § 3 for spheres of central structure, § 4 for ellipsoids, cf. also p. 255 note 1 of that Suppl.) and VAN DER WAALS attractive forces. This assumption gives

$$B_N = b_{WN} \left\{ 1 - \frac{a_{WN}}{b_{WN}R_N T} \right\} \dots \dots \dots (3)$$

(cf. Suppl. N<sup>o</sup>. 24a § 3 equation (14)), where  $a_{WN}$ ,  $b_{WN}$  and  $R_N$  are constants. For this investigation  $\mathcal{F}'_1 = \log(1-\tau)$ , in which  $\tau = \frac{a_{WN}}{b_{WN}R_N T}$  is now plotted as a function of  $\log \tau$  on transparent squared paper to the same scale as before. But  $\log \tau$  is now taken as increasing in the opposite direction to that in which  $\log T$  increases in the previous diagrams.

For comparison with the assumption that the molecules of a gas behave as if they were rigid molecules of central structure each with an electric doublet of constant moment at its centre, equation (59) of Suppl. N<sup>o</sup>. 24b § 6 was written in the form :

$$B_N = b_{WN\infty} \left\{ 1 - \frac{1}{3} (hv)^2 - \frac{1}{75} (hv)^4 - \frac{29}{55125} (hv)^6 \dots \right\} \dots \quad (4)$$

Here  $h$  and  $v$  have the same significance as in Suppl. N<sup>o</sup>. 24b § 6, and  $b_{WN\infty}$  is the factor which, for the units now employed, must replace the factor  $\frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3$  of Suppl. N<sup>o</sup>. 24b § 6.

$$\mathcal{F}_2 = \log \left\{ 1 - \frac{1}{3} (hv)^2 - \frac{1}{75} (hv)^4 - \frac{29}{55125} (hv)^6 \dots \right\} \quad (5)$$

is now plotted as a function of  $\log hv$ , where again  $\log hv$  is taken increasing in the direction opposite to that in which  $\log T$  increases in the  $\log B_N, \log T$ -graph. Where necessary in (5) terms up to and including  $(hv)^{12}$  were used in the calculation.

As in Suppl. N<sup>o</sup>. 23 Nr. **38** (cf. note 399 of that Suppl.) where the argument of the logarithm is negative, the absolute value of the logarithm is plotted, and the corresponding portion of the curve is marked by (*n*).

To ascertain if the experimental values of  $B_N$  correspond to one or other of the equations (3) and (4), is now the same as trying if the corresponding  $\log B_N, \log T$ -curve can be made to coincide as a whole or in part with the corresponding  $\mathcal{F}_1, \log \tau$ , or  $\mathcal{F}_2, \log hv$ -curve by moving it over the other, keeping the coordinate axes of the two graphs constantly parallel<sup>1)</sup>.

§ 3. *Hydrogen. a.* The individual virial coefficients for hydrogen were taken from Comm. N<sup>o</sup>. 100*a* (Dec. '07) table XXII and from Comm. N<sup>o</sup>. 100*b* (Dec. '07) by KAMERLINGH ONNES and BRAAK (cf. Comm. N<sup>o</sup>. 101*b* (Dec. '07) table XXV for the reduction of the temperatures to the AVOGADRO scale), and from Comm. N<sup>o</sup>. 127*c* (these Proceedings) table IV by KAMERLINGH ONNES and W. J. DE HAAS<sup>2)</sup>.

*b.* On moving the  $\log B_N, \log T$ -diagram for hydrogen over the  $\log \mathcal{F}_1, \log \tau$ -diagram, which I shall call in what follows the diagram for  $a_W$  and  $b_W$  constant, it was evident that it was not possible to get them to coincide over any extensive temperature region (see fig. 1). From this it is again (cf. Suppl. N<sup>o</sup>. 23 Nr. **44** for the general case) evident that constant values of  $a_W$  and  $b_W$  cannot be used to represent even the planetary gas state (which, cf. Comm. N<sup>o</sup>. 127*c*, these Proceedings, § 1 by KAMERLINGH ONNES and W. J. DE HAAS, can be more closely defined as that state in which only the  $B$ -term is still of influence in the equation of state) for hydrogen, over a temperature region of any appreciable extent.

One could now try to determine values of  $a_W$  and  $b_W$  which on the assumption that  $a_W$  and  $b_W$  are constant over any limited region

<sup>1)</sup> This method corresponds to the  $\log B, d \log B / d \log T$ -method of Suppl. N<sup>o</sup>. 23 note 399.

<sup>2)</sup> The individual virial coefficients for hydrogen calculated from the observations of AMAGAT, and given in Comm. N<sup>o</sup>. 71, June '01, p. 143, do not agree sufficiently with those given by the Leiden measurements and are therefore unsuitable for extending the temperature variation of  $B_N$  to higher temperatures.

of temperature for these regions would give by equation (3) values of  $B$  in sufficiently good agreement with the experimental values; this is done by so moving the curves with respect to each other that the curve joining the experimental points touches the  $T_1, \log \tau$ -curve within the limits of each particular region<sup>1)</sup>. In fig. 1 the one curve is moved over the other so as to give agreement at the BOYLE-point<sup>2)</sup>.

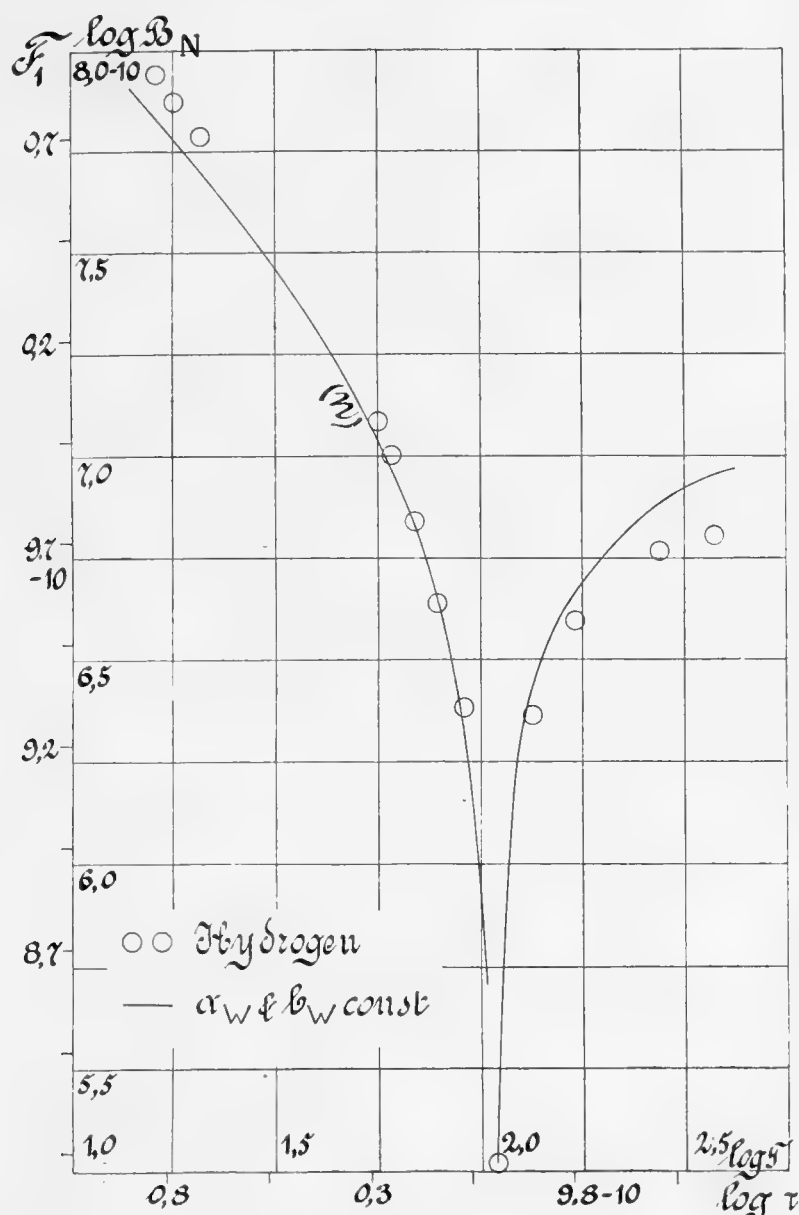


Fig. 1.

In this the point  $\log T = 2,0$ ,  $\log B_N = 6,5-10$  coincided with the point  $\log \tau = 0,024$ ,  $T_1 = 9,412-10$ . From this in conjunction with  $A_{N0^{\circ}C} = A_{A0(71)} = 0,99942$ <sup>3)</sup> we find  $a_{WN} = 0,473 \cdot 10^{-3}$  and  $b_{WN} =$

<sup>1)</sup> With these values of  $a_W$  and  $b_W$  we could, as in Suppl. No. 23 Nr. 38, for each temperature determine values of the critical reduction quantities for the planetary gas state of the substance under investigation, if we choose as standard for comparison a fictitious substance whose  $a_W$  and  $b_W$  are assumed to be constant.

<sup>2)</sup> One can easily see how the criterion of contact must be modified for this case.

<sup>3)</sup> In Comm. No. 100b, Dec. '07, 0.99924 is printed by mistake (as is at once seen from the value of  $B_{A0(71)}$ ).

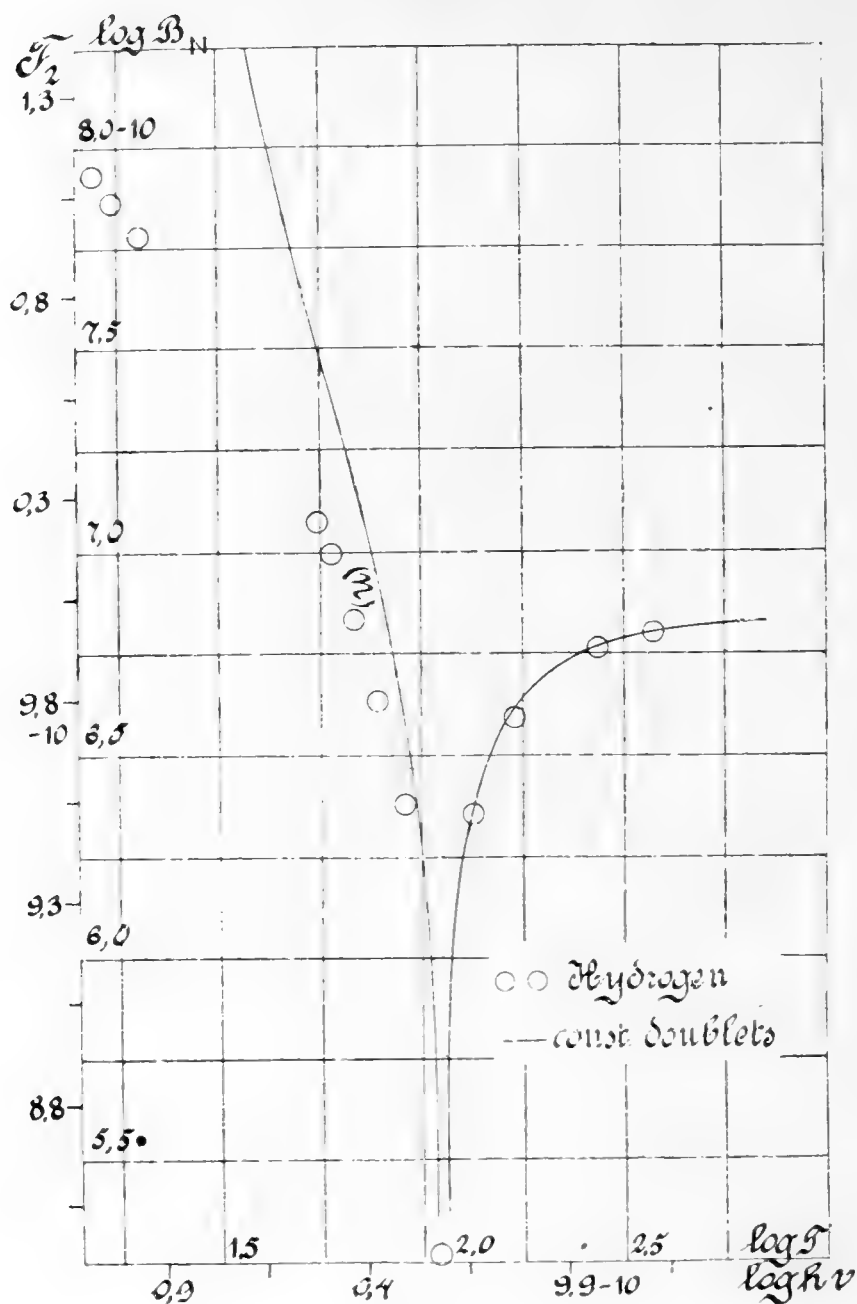


Fig. 2.

$1,224 \cdot 10^{-3}$ ; these values, therefore, on the assumption that these magnitudes are constant, will give the closest possible agreement with the experimental thermal equation of state, at least for the planetary gas state, at the particular temperature under consideration, which is here found to be  $106^\circ \text{K}$ .<sup>1) 2)</sup>

1) The values of  $a_{wN}$  and  $b_{wN}$  given by BRAAK, Diss. Leiden 1908, p. 82 were obtained by a method of calculation which is essentially the same as the  $\log B$ ,  $\lg C$ -method of Suppl. No. 23, Nr. 38, applied to the comparison of hydrogen with a fictitious standard with constant  $a_w$  and  $b_w$ . The difference between these and the results obtained by the  $\log B$ ,  $d \log B / d \log T$ -method here, show that complete correspondence does not exist between hydrogen and the fictitious standard with constant  $a_w$  and  $b_w$  even over a limited temperature region, if one is not confined to the planetary state.

2) The deduction of similar values of  $a_w$  and  $b_w$  for other temperatures which might be followed by the development of deviation functions as for instance indicated in Suppl. No. 23, Nr. 38, was not made.

c. On moving the  $\log B_N$ ,  $\log T$ -diagram for  $H_2$  over the  $\mathcal{F}_2$ ,  $\log hv$ -diagram, which I shall refer to henceforth as the diagram for constant doublets, it was found that comparatively good coincidence was obtained at temperatures above the BOYLE point, see Fig. 2. At temperatures below the BOYLE point, differences, which begin to be noticeable even at the point  $-164^\circ C.$  still above the BOYLE point, become very marked, so that below a certain temperature not even local coincidence (contact between the two curves) can be obtained.

If we look upon these differences at the lower temperatures as a consequence of a deviation, which increases regularly towards those temperatures, of the behaviour of the  $H_2$ -molecules from that which is assumed in the hypotheses from which the constant doublets diagram is constructed, there is then reason for superposing the diagrams in a manner slightly different from that shown in Fig. 2, viz. so that the points indicating the highest observed temperatures should lie upon the curve of constant doublets. The  $\log B_N$ ,  $\log T$ -diagram does then, in fact, exhibit a deviation from the constant doublets diagram, increasing regularly towards the lower temperatures, and already appreciable at  $-139^\circ C.$  At higher temperatures as far as the observations extend, that is, up to  $100^\circ C.$ , and taking into account the accuracy with which  $B$  can be deduced from the observations, we may say that as far as  $B$  is concerned *the thermal behaviour of hydrogen in the planetary gas state may be represented by that of a system of rigid spheres of central structure, each with an electric doublet of constant moment at its centre.* The caloric behaviour of  $H_2$ , in which differences clearly occur earlier, is, to a first approximation, consistent with this at the higher temperatures of the region under consideration.

From this method of superposing the diagrams we may easily deduce values of  $\sigma$ , the diameter of a molecule, and of  $v$ , the potential energy ( $v$  being 0 for  $r = \infty$ ) of two molecules in contact, when the axes of the doublets are respectively parallel and perpendicular to the line joining the centres of the molecules (cf. Suppl. N<sup>o</sup>. 24b § 6). On superposing them so that the  $H_2$ -points for the highest three temperatures fell upon the line for constant doublets, then the point  $\log hv = 0,2$ ,  $\mathcal{F}_2 = 9,7-10$  coincided with the point  $\log T = 2,075$ ,  $\log B_N = 6,540-10$ . From this, together with the value  $k_P = 1,21 \cdot 10^{-16}$  (Suppl. N<sup>o</sup>. 23, note 174) taken from PERRIN'S observations we obtain

$$v = 2,28 \cdot 10^{-14} \text{ [erg].}$$

From this too, we get for four times the molecules own volume

on the assumptions here made, expressed in terms of the normal volume as unit,  $b_{WN\infty} = 0.692 \cdot 10^{-3}$ . This value, which can also be regarded as to be obtained by extrapolation to very high temperatures, is markedly smaller than the value obtained above on the assumption that  $a_W$  and  $b_W$  may be regarded as constant over a small region of temperature, and it is also much smaller than that given by BRAAK, Diss. p. 82 and 83. We shall return to the variation of  $b_W$  with the temperature when we come to consider the viscosity.

From  $b_{WN\infty}$  we obtain the diameter of the molecule using the relation

$$b_{WN\infty} A_{N_0^{\circ}C} \Theta_M = \frac{1}{2} N \cdot \frac{4}{3} \pi \sigma^3. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In this  $\Theta_M = 22413$  [ $\text{cm}^3$ .]<sup>1)</sup> is the theoretical normal volume of the gram molecule, and  $N = 6,85 \cdot 10^{23}$ <sup>2)</sup> is the AVOGADRO number. We find

$$\sigma = 2,21 \cdot 10^{-8} \text{ [cm.]}$$

From the values of  $v$  and  $\sigma$  we further obtain the moment of the doublet

$$m_e = 4,96 \cdot 10^{-19} \text{ [electrostatic unit. cm.]}$$

Assuming that each pole bears a charge equal to that of a single electron, the distance between the poles should be  $1,17 \cdot 10^{-9}$  cm.<sup>3)</sup>, that is, about one twentieth of the diameter of a molecule; within the interior of a molecule there is therefore plenty of room for such a doublet. At the temperatures here considered the mean speeds of rotation assumed by the molecules are such that the electromagnetic force exerted by the molecules upon each other need not be taken into account, and this confirms the assumption previously made

1) Cf. Suppl. N<sup>o</sup>. 23, note 23, and "Einheiten" *a*.

2) Taken from PERRIN's researches; cf. Suppl. N<sup>o</sup>. 23, note 173.

3) From the energy required to ionise the gas RUTHERFORD and MC KLING, Physik. ZS. 2 (1900), p. 53, obtained the same order of magnitude. So, too, did REINGANUM, Physik. ZS. 2 (1900), p. 241, Ann. d. Phys. (4) 10 (1903), p. 334, and loc. cit. p. 417 note 1, from the dependence of viscosity upon temperature (cf. § 6), from the tensile strength of metals, and from the latent heats of vaporisation of liquids, while the same order of magnitude for the moment of the molecule was obtained by DEBIJE, Physik. ZS. 13 (1912), p. 97, from the variation with temperature of the dielectric constants of certain liquids.



(Suppl. N<sup>o</sup>. 24b § 6), that we need only allow for electrostatic forces.<sup>1)</sup>

Consideration of the viscosity lends some support to the result obtained above that hydrogen behaves at higher temperatures in the planetary gas state as a system of hard spheres of central symmetry, each with an electric doublet at its centre, but deviating considerably therefrom at lower temperatures. On this point we may refer to § 6.

d. Comparison of the  $\log B$ ,  $\log T$ -diagram for hydrogen with that for argon affords an important insight into the behaviour of  $H_2$  below the BOYLE point which is closely related to the deviation found in c for the  $H_2$  diagram from that for constant doublets<sup>2)</sup>. The

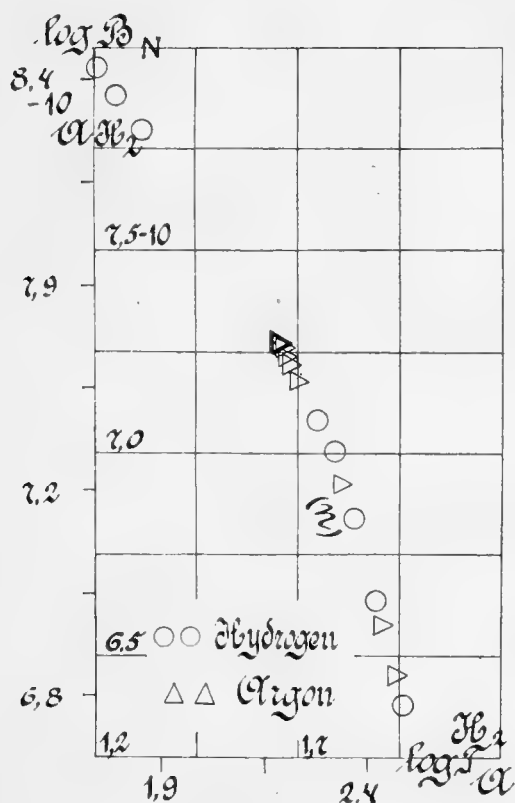


Fig. 3.

individual virial coefficients for argon were taken from Comm. N<sup>o</sup>. 118b (Dec. 1910) by KAMERLINGH ONNES and CROMMELIN. From their measurements a portion of the branch ( $n$ ) of the  $\log B$ ,  $\log T$ -curve lying below the BOYLE point is accurately known.

On superposing the  $\log B_N$ ,  $\log T$ -curve for hydrogen on that for argon it is evident that the latter quite well fits the corresponding part of the hydrogen curve, see Fig. 3<sup>3)</sup>.

From this it follows that, in so far as the second virial coefficient of the thermal equation of state is concerned, the thermal behaviour of hydrogen from  $-180^\circ \text{C.}$  to at least  $-230^\circ \text{C.}$  (the temperature for hydrogen which corre-

<sup>1)</sup> The length of the axis of a doublet may also be neglected in a first approximation, as has always been done here. In a more accurate calculation, however, this would have to be allowed for.

<sup>2)</sup> The deviations from the law of corresponding states occurring in  $B$  and  $C$  for hydrogen when compared with their values for other substances, such as oxygen, nitrogen, carbon dioxide, ether and isopentane, for which, as well as for hydrogen at very high reduced temperatures, the mean reduced equation VII.1 (Suppl. N<sup>o</sup>. 19, p. 18) holds, first found definite expression in the special equation VII.H<sub>2</sub>.3 (Comm. N<sup>o</sup>. 109a equ. (16)), which was introduced for this purpose; marked differences occur between the  $\mathfrak{B}$  and  $\mathfrak{C}$  of this special equation and those of the mean equation VII.1. The continuation of the investigation of the nature of these differences which was commenced in Suppl. N<sup>o</sup>. 23, Nr. 38, was left to me by Prof. KAMERLINGH ONNES.

<sup>3)</sup> Then the point  $\log T = 2.4$ ,  $\log B_N = 7.2-10$  for argon coincided with the point  $\log T = 1.869$ ,  $\log B_N = 6.908$  for hydrogen.

sponds to the lowest observed argon temperature) *corresponds to that of a monatomic substance*<sup>1) 2)</sup>.

*e.* In Nr. **38** of Suppl. N<sup>o</sup>. 23 hydrogen is compared with helium. From fig. 15 of that Suppl. it is evident that from the BOYLE point downwards good correspondence is obtained between He and H<sub>2</sub> in so far as any conclusion is possible from the small number of helium points which were available for the construction of that particular branch of the  $\log B, \log T$ -curve<sup>3)</sup>. To the figure just quoted we may now add the helium point 4<sup>o</sup>,29 K. from Comm. N<sup>o</sup>. 119 (March 1911) § 5, which, in that figure, comes above the argon-hydrogen line. A suitable displacement<sup>4)</sup>, however, of the helium diagram brings this point (whose degree of accuracy, however, is not so high as that of the points forming the H<sub>2</sub>-A-curve), too, on to the hydrogen-argon curve.

From fig. 16 of Suppl. N<sup>o</sup>. 23 one can see further that, when superposing the hydrogen and helium curves so that the branches below the BOYLE point coincide, those above the BOYLE point deviate markedly from each other, from the figure quoted and from the table referring to it in note 399, that coincidence between the branches above the BOYLE point can be obtained only over a very limited region<sup>5)</sup>. So that at these higher temperatures appreciable deviations from correspondence between He and H<sub>2</sub> exist.

1) The preliminary values of  $B_N$  obtained for helium in the corresponding region do not conflict with the suspicion that this is the case down to much lower temperatures (see *e*).

2) From the data given on p. 425 note 3 for the displacement necessary to obtain coincidence between the A-curve and the H<sub>2</sub>-curve, and from the value  $T_k = 150.65$  for argon (G. A. CROMMELIN, Comm. N<sup>o</sup>. 115, May 1910), we can calculate  $T_{kr(H_2:A)} = 25,25$  for the critical reduction temperature for hydrogen with respect to argon as standard for comparison (cf. Suppl. No. 23, Nr. **38b**). Comparison with the critical temperature for hydrogen on the one side, with  $T_{kr(H_2:N_2,O_2)} = 43$  (Suppl. No. 23 note 399) on the other side leads to the conclusion that the virial coefficients for hydrogen and argon higher than the second do not correspond perfectly, though the deviation from correspondence between the two substances within the region of temperature under consideration is much smaller than that between H<sub>2</sub> and N<sub>2</sub> or O<sub>2</sub>.

3) The third virial coefficient,  $C$ , then corresponds as well (see fig. quoted). In good agreement with this is the finding of a constant value for  $T_{kr(He:H_2)}$ , at the points  $t_{He} = -253^o$  and  $-259^o$ , which does not differ much from  $T_k He$  (Suppl. No. 23 note 399).

4) In this there is no longer any notice taken of the correspondence between the  $C$  coefficients, as is also the case in the other diagrams discussed in the present paper.

5) Comparison with fig. 15 shows that the third virial coefficient,  $C$ , would then exhibit wide deviations from correspondence.

*f.* If we combine the results obtained in *d* and *e* with those given in *c* we reach the conclusion that, as far as *B* is concerned, *between*  $-100^{\circ}\text{C.}$  and  $-180^{\circ}\text{C.}$  *the thermal behaviour of hydrogen*, which, between  $-100^{\circ}\text{C.}$  and  $+100^{\circ}\text{C.}$  is that of a system of rigid spheres of central structure each with an electric doublet of constant moment at its centre, and acting upon each other according to the ordinary laws of mechanics and of the electromagnetic field, now *changes to that which characterises a monatomic substance*, and that between  $-180^{\circ}\text{C.}$  to at least  $-230^{\circ}\text{C.}$  this behaviour is completely followed <sup>1)</sup>. On this account we shall postpone further considerations of the second virial coefficient for hydrogen in this region until monatomic gases are discussed in a subsequent communication.

From the above it is accordingly evident that the thermal behaviour of hydrogen exhibits a strict parallelism with its caloric behaviour as deduced from EUCKEN'S measurements of the specific heat at constant volume. As we suspect, in accordance with the theories of NERNST <sup>2)</sup> and EINSTEIN <sup>3)</sup>, that the decrease in the specific heat at lower temperatures will find an explanation in the application of the hypothesis of finite elements of action to the rotations of the molecule, the parallelism here observed at once leads to the question as to whether the explanation of the peculiarities of the thermal equation of state for hydrogen obtained in the present paper may not profitably be sought in the same direction. For instance, one can imagine that the hypothesis in question would lead to the assumption that, on approaching one another, the molecules have not such orientations and are not so distributed with respect to their mutual distances, as is required by the laws of statistical mechanics according to ordinary dynamics and electrodynamics, and that therefore the mean attraction would be smaller at lower temperatures <sup>4)</sup> than would be the case if these laws were obeyed at these temperatures as well.

From the fact that *B* is negative at those temperatures at which the di-atomic hydrogen begins to behave as a monatomic substance, and that there is consequently some attraction still left which does not decrease much more even with the temperature (cf. *b*), it follows that the quantum hypothesis applied to this region would not have

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<sup>1)</sup> The temperature regions here given are not to be regarded as sharply bounded, still less are they to be considered as sharply defined by the observations at present available.

<sup>2)</sup> W. NERNST. ZS. f. Elektrochem. 17 (1911), p. 265.

<sup>3)</sup> A. EINSTEIN. Discussions of the SOLVAY Congress, Nov. 1911.

<sup>4)</sup> A similar diminution of the attraction was assumed in Comm. No. 119 in order to explain the maximum observed in the density of helium.

to lead to a large decrease of the whole of the attraction, but only to that of a part of it. This, then, would again lead to the hypothesis that at higher temperatures only part of the attraction is to be ascribed to the mutual action of the doublets of constant moment, another part being ascribed to a mutual action of the molecules corresponding to the mutual attraction of monatomic molecules (cf. Suppl. N<sup>o</sup>. 23 Nr. 34*d*). The answer to the question as to whether treatment on these lines would lead to a still better agreement with observation than that obtained in *c* must, in the meantime, be postponed till a later Communication.

§ 4. *Oxygen*<sup>1)</sup>. The individual virial coefficients for oxygen were taken from Comm. N<sup>o</sup>. 71, p. 143.

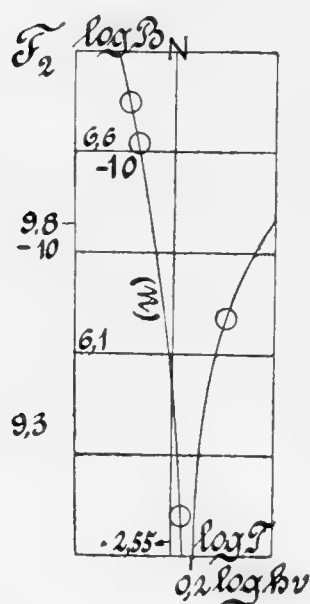


Fig. 4.

From Fig. 4 it is evident that the oxygen points (oo) lie well upon the curve (—) for constant doublets, so that in this particular region (0°—200° C.), as far as *B* is concerned, and subject to the reserve of note 1, the behaviour of oxygen may be regarded as that of a system of rigid spheres of central structure each with a doublet of constant moment at its centre. From the following data concerning the superposition of the diagrams (cf § 3*c*) we obtain the accompanying results: the point  $\log T = 2,6$ ,  $\log B_N = 6,5 - 10$  for oxygen coincides with the point  $\log h v = 0,204$ ,  $F_2 = 9,628 - 10$  on the curve for constant doublets, hence:

$$v = 7,71 \cdot 10^{-14}, \quad b_{WN\infty} = 0,745 \cdot 10^{-3}, \quad \sigma = 2,27 \cdot 10^{-8}, \quad m_c = 9,47 \cdot 10^{-19}.$$

On the assumption that each of the poles of the doublet bears a charge equal to that carried by a single electron, the length of its axis should consequently be one tenth of the diameter of the molecule. The oxygen molecule should accordingly be about as large as the hydrogen molecule, but the moment of its doublet should be about twice as great as that of the hydrogen doublet.

§ 5. *Nitrogen*<sup>1)</sup>. The individual virial coefficients deduced from

<sup>1)</sup> The lack of agreement between the observations of KAMERLINGH ONNES and BRAAK upon hydrogen and those of AMAGAT (cf. p. 420, note 2) shows how desirable it is that new observations should extend our experimental data over a wider range of temperature and give a control upon the values of *B* deduced from AMAGAT's data for oxygen and nitrogen as well as for hydrogen. In the meantime

AMAGAT's observations covering the region  $0^\circ$  tot  $200^\circ$  C. were taken from Comm. No. 71, p. 143. From the observations of BESTELMEYER and VALENTINER<sup>1)</sup> it is possible to obtain still another value for  $B_N$ . At  $T = 81,01$  we get  $B_{N(71)} = -3,411 \cdot 10^{-3}$ , from which with (2)  $B_N$  follows.

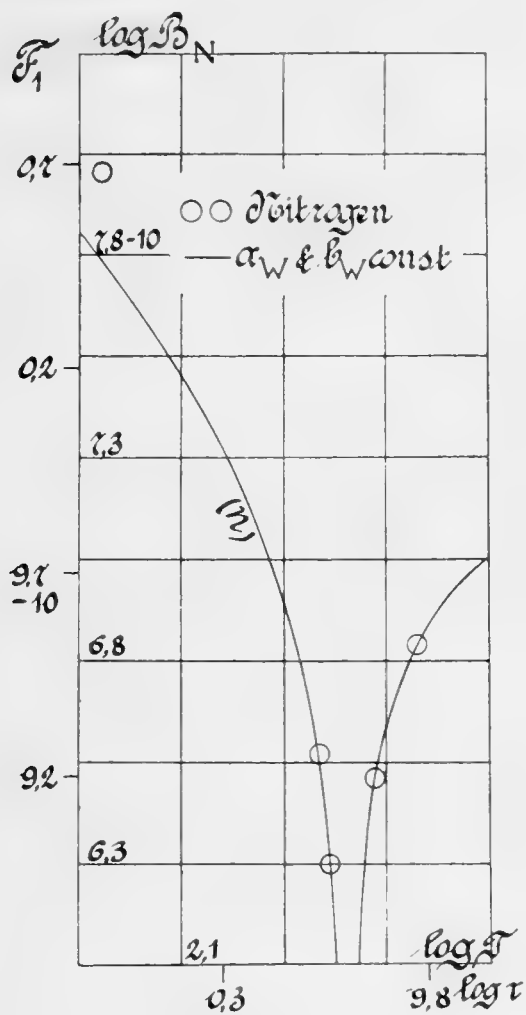


Fig. 5.

Comparison of the nitrogen diagram with the curve for constant doublets and with the hydrogen diagram shows that nitrogen deviates markedly from the other two especially in the neighbourhood of the BOYLE-point<sup>2)</sup>. Comparison with the curve for  $a_W$  and  $b_W$  constant shows that the four points taken from AMAGAT's observations can be brought into pretty close agreement with the curve, while the point given by BESTELMEYER and VALENTINER lies then pretty far above it (see Fig. 5). In Fig. 5 the point

$\log \tau = 0,004$ ,  $\mathcal{F}_1 = 9,731 - 10$  coincides with the point

$\log T = 2,5$ ,  $\log B_N = 7,05$ ,  
from which we get, for the region covered by AMAGAT's observations:  
 $a_{WN} = 2,44 \cdot 10^{-3}$ ,  $b_{WN} = 2,08 \cdot 10^{-3}$ .

§ 6. *Coefficient of viscosity*<sup>3)</sup>. It seemed of importance to investigate whether the results obtained in § 3 find confirmation or not in the manner in which the coefficient of viscosity varies with the temperature. The second column of the following Table, which, on

it appeared not quite devoid of interest to utilise the data at present available for these two gases subject to such reserve as may be necessitated by future control and extension, for comparing with the results of Suppl. N<sup>o</sup>. 24.

<sup>1)</sup> A. BESTELMEYER and S. VALENTINER. Ann. d. Phys. (4) 15 (1904), p. 72.

<sup>2)</sup> The different behaviours of  $N_2$  and  $O_2$  from the point of view of the law of corresponding states was illustrated by the two corresponding Tables of Comm. No. 71. The influence of the magnetic properties of oxygen will be investigated later.

<sup>3)</sup> An investigation of viscosity at low temperatures has been in progress at Leiden for some time. Papers by KAMERLINGH ONNES and DORSMAN on the viscosity of hydrogen and by KAMERLINGH ONNES and S. WEBER on helium will soon be published.

the theory of rigid spheres without attraction, should show the figure 1,000 at each temperature, gives results taken from the observations of MARKOWSKI<sup>1)</sup> and of KOPSCH<sup>2)</sup>; in column 3,  $b_W$  is the quantity which, multiplied by the factor  $\frac{3}{2} \frac{RT}{v}$ , gives the collision virial; in accordance with the splitting indicated in Suppl. N<sup>o</sup>. 24b § 6 of the whole virial of the mutual forces between the molecules into the collision virial and the attraction virial,  $b_{W0^{\circ}C.}/b_W$  is calculated from<sup>3)</sup>

$$b_W = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \left\{ 1 + \frac{1}{3!} q_1 (h\nu)^2 + \frac{1}{5!} q_2 (h\nu)^4 + \frac{1}{7!} q_3 (h\nu)^6 \dots \right\} \quad (7)$$

(for  $q_1, q_2 \dots$  see Suppl. N<sup>o</sup>. 24b § 6), or

$$b_W = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \left\{ 1 + \frac{1}{3} (h\nu)^2 + \frac{1}{25} (h\nu)^4 + \frac{29}{11025} (h\nu)^6 \dots \right\} \quad (8)$$

Although the theory of viscosity, and, in particular, of the influence of molecular attraction upon it, is not yet sufficiently worked out to draw quite certain conclusions therefrom, yet comparison of these two columns seems to show that the behaviour of hydrogen above 0° C. is in pretty good agreement with that of a system of rigid spheres of central structure each with an electric doublet of

$t$	$\frac{\eta}{\eta_{0^{\circ}C}} \sqrt{\frac{T_{0^{\circ}C}}{T}}$ hydrogen	$\frac{b_{W0^{\circ}C.}}{b_W}$ const. doublets
184.2	1.408	1.104
100.5	1.058	1.074
0	1.000	1.000
- 78.73	0.940	0.865
-194.9	0.827	0.236

constant moment at its centre, but that below 0° C. it deviates considerably therefrom. Comparison of hydrogen and argon shows that

<sup>1)</sup> H. MARKOWSKI. Ann. d. Phys. (4) 14 (1904), p. 742,

<sup>2)</sup> W. KOPSCH. Diss. Halle 1909.

<sup>3)</sup> For the corresponding  $a_W$  we obtain a series with only odd powers of  $h\nu$  beginning with the first; the first term is consequently proportional to  $T^{-1}$  (cf. Suppl. No. 23, Nr. 48c) while the subsequent terms become small with comparative rapidity.

the viscosity of hydrogen at  $-192.7^{\circ}\text{C}$ . and that of argon at  $0^{\circ}\text{C}$ . deviate from correspondence by only 6% (taking the coefficients of similarity from § 3 *d*), but that the viscosity of hydrogen from  $-193^{\circ}\text{C}$ . upwards increases much more slowly with the temperature (corresponding to a more rapid increase in the attraction in the case of hydrogen within the region of transition) than corresponds to the increase in the viscosity of argon. This confirms in some degree the conclusions reached in § 3.

Confirmation would have been attained in a higher degree if corresponding to § 4 agreement had been obtained between the temperature variation of the viscosity of oxygen and  $b_{\text{W } 0^{\circ}\text{C.}}/b_{\text{W}}$  as given by (8), using the value of  $v$  obtained in § 4. This, however, is not at all the case. That temperature variation can, indeed, as far as observations<sup>1)</sup> go, be represented with the aid of  $b_{\text{W}}^{-1}$  of (8) but then we find  $v = 2,79 \cdot 10^{-14}$  instead of the  $7,71 \cdot 10^{-14}$  deduced in § 4 from the coefficient  $B$ . Unless the agreement obtained in § 4 is wholly fortuitous we must conclude from this that a deviation from the temperature variation of the viscosity of oxygen as deduced upon the assumption of rigid spheres each with a constant doublet at its centre is occasioned by some circumstance whose influence upon  $B$  vanishes, or is at least extremely small. As such, for instance, one could regard deviations from sphericity in the molecular shape.

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<sup>1)</sup> By H. MARKOWSKI. p. 430, note 1. (The observations by E. VÖLKER, Diss. Halle 1910, on the coefficient of viscosity of  $\text{O}_2$  down to  $-152^{\circ}.52\text{C}$ ., which came to my notice only after the Dutch original of this paper was printed, join those observations at  $0^{\circ}$ — $14^{\circ}.65\text{C}$ . Below  $0^{\circ}\text{C}$ . they show a deviation from  $b_{\text{W}}^{-1}$  for constant doublets in the same sense as that exhibited by  $\text{H}_2$ . At  $-40^{\circ}\text{C}$ . this deviation is already distinct and it finally becomes very marked. (Added in the English translation).

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### E R R A T A.

In the Proceedings of the meeting of June 29, 1912.

- p. 258 l. 9 from the top: for micro-complexion read macro-complexion,  
 p. 261 l. 1 ,, ,, bottom: for  $u_{w_1} - h \{ \frac{1}{2} \varphi(r_1) \}$  read  $h \{ u_{w_1} - \frac{1}{2} \varphi(r_1) \}$ .  
 p. 266 l. 5 ,, ,, top: for  $\infty$  read  $\tau$ .  
 p. 271 l. 13 ,, ,, bottom: for  $EBD$  read  $EBB'$ .
- 

**(October 24, 1912).**





KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING  
of Saturday October 26, 1912.

*President:* Prof. H. A. LORENTZ.

*Secretary:* Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 26 October 1912, Dl. XXI).

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**Biochemistry.** — “*The antagonism between citrates and calciumsalts in milkcurdling by rennet. A contribution to the knowledge of the relation between structure and biological action*”. (First communication). By J. R. KATZ. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of April 26, 1912).

### *Introduction.*

A small quantity of neutral citrates prevents the coagulation of blood; various salts which precipitate calcium as an insoluble compound, e.g. oxalates and fluorides, have an analogous action. The peculiarity of the case is however that citrates do not precipitate diluted solutions of calciumsalts, but remain entirely clear; notwithstanding this, they have neutralized the effect of the calcium.

A similar antagonism between citrates and calcium has been found in various biochemical and pharmacological processes.

Citrates in small quantity prevent the curdling of milk by rennet; various immunochemical reactions are prevented by citrates, as the laking of red bloodcorpuscles by animal hemolysines (eelserum cobralecithide, normal complement); here also the action of citrates is prevented by the addition of calciumsalt<sup>1)</sup>.

Recently Prof. HAMBURGRR has shown that the phagocytic power of the leucocytes is inhibited by citrates and is reactivated by calciumsalts and that fluorides and oxalates too prevent phagocytosis.

The pharmacological action of citrates shows the same antagonism with calciumsalts, e.g. JANUSHKE<sup>2)</sup> has found that the paralysis of the heart and the paralysis of the nervous system caused by intravenous injection of citrates, is removed by injection of calcium. BUSQ and PACHON<sup>3)</sup> showed, that there exists antagonism between the action of citrates and calcium on the heartmuscle, and MAC CALLUM<sup>4)</sup> observed that the purgative action of citrates is inhibited by addition of calciumsalt.

It seems perfectly clear, that substances as fluorides and oxalates which precipitate calcium as a nearly insoluble compound, are antagonists of calcium, but how shall we explain, that citrates have the same action, although they do not precipitate calciumsalt?

As this property of citrates is used more and more in hema-

<sup>1)</sup> GENGOU, Arch. Intern. de Physiologie 7 (1903).

<sup>2)</sup> Arch. f. Exper. Pathol. u. Pharmak. 61. p. 363—375.

<sup>3)</sup> C. R. 148 p. 575—578.

<sup>4)</sup> Americ. Journ. of Physiol. 10, p. 101—110.

tological and immunochemical reactions, it has drawn attention from various sides. SABBATANI <sup>1)</sup> thinks, that its action might be caused by the diminution of the number of free calciumions; ARTHUS <sup>2)</sup> and GENGOU <sup>3)</sup> showed, that citrates have an antiflocculant action on finely divided suspensions, and asked whether the biological action should not rather be attributed to the latter. Finally M. H. FISCHER <sup>4)</sup> proved recently that citrates inhibit to a large extent the swelling (imbibition) of proteids by acids and by alkalis and that some pharmacological properties of these salts (e.g. their influence on glaucoma) are related to this. Each of these theories is supported by a number of experiments; possibly all three contain a part of the truth; under these circumstances a choice between the different explanations does not seem possible as long as the biological action of citrates has not been more extensively analysed.

*Analysis of the biological action of citrates by comparison  
with the action of substituted citrates.*

For such an analysis the finding of the active groups in the citrate-molecule seems particularly adapted. For it seems rather improbable that the different actions of the citrates are all caused by the same groups. Then this research will give an indication which actions can be compared, which not.

In order to find which are these groups, I have followed the ordinary pharmacological method. A number of derivatives of citric acid were prepared in which the probably active groups were changed in different ways. As all acids which precipitate calcium in the manner of fluorides and oxalates inhibit the curdling of milk, this secondary complication should be excluded. On this account I have made a control with all acids examined in order to see if the solution of the neutral salt of the acid used, precipitated a diluted solution of calciumsalt. Only those, which did not were used for the investigation. As solution of calciumsalt I chose a solution of gypsum (saturated solution, diluted 1 : 5 with distilled water).



Citric acid,  $\text{COOH} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CH}_2 \cdot \text{COOH}$ , contains 4 groups which may be considered as the active ones: three carboxylgroups COOH and one alcoholgroup OH. The hydroxylgroup can be made inactive

<sup>1)</sup> Atti della R. Acad. di Torino **36**, p. 27—53; Memorie [2] **52**, p. 213—257.

<sup>2)</sup> C. R. Soc. de Biol. **36** (1901).

<sup>3)</sup> l. c.

<sup>4)</sup> Das Oedem.

by acetylation; of the carboxylgroups one, two, or three can be removed by preparing the mono-, di- and tri-amides, or mono-, di- and tri-esters<sup>1)</sup>.

a. *The alcoholgroup made inactive.*



Anhydrous citric acid was boiled with acetylchloride according to EASTERFELD and SELL<sup>2)</sup>; the acetylcitric anhydride formed is purified by washing with acetylchloride and dried in the exsiccator above sodium hydroxide. Immediately before use, this substance was recrystallised with chloroform until it had the exact melting-point. A weighed quantity of this substance was dissolved in water of 50° C., when the anhydride changes into acetylcitric acid, and then was neutralized with titrated sodium hydroxide solution. Three equivalents of sodium hydroxide were used pro molecule acetyl-citric anhydride, as should be the case when no acetic acid is split off. Such a solution is relatively very stable at ordinary temperature and only becomes acid after several weeks (by breaking up into acetic acid and citric acid).

When the alcohol-group of citric acid is made inactive, the substance has become comparable with other multi-basic aliphatical acids without alcohol group. It therefore is interesting to compare some of these acids with acetylcitric acid as to their action on milk-curdling<sup>3)</sup>.

For comparison were chosen:



Purity controlled by melting point.



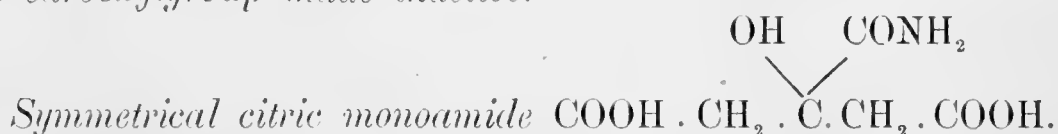
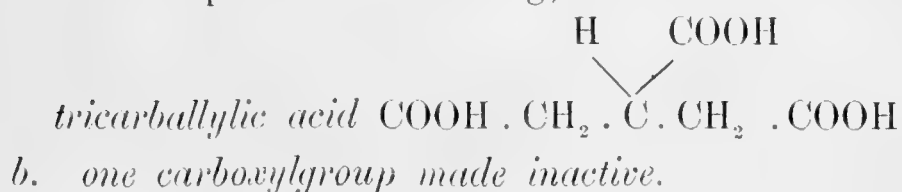
The tetra-ethylester of this acid was prepared by condensation of malonic ester with 2 molecules of monochlor-acetic-

1) I am indebted to Dr. J. BLANKSMA for his amiable advice in synthetical difficulties.

2) Journ. of the Chem. Soc. **61**, p. 1003—1012.

3) In order to prevent secondary complications I have for comparison chosen acids which differ as little as possible in structure from the original ones. Acids in which the carboxylgroups are nearer to one another than in the citric acid-molecule were excluded, because in such cases other properties so often appear.

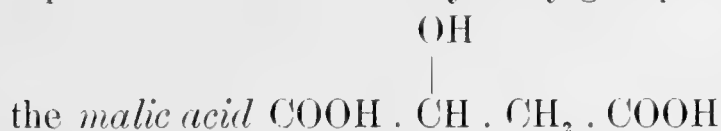
acid ester. This tetra-ethylester was saponified in alcoholic solution according to the method of BISCHOFF<sup>1)</sup>; addition of BaCl<sub>2</sub> precipitated the bariumsalt. This starchy looking salt could not be sucked dry; it was purified by repeated decantation. The free acid was prepared by adding the calculated quantity of sulphuric acid; it was extracted with ether and recrystallised with anhydrous ether until it had the right melting-point (this never was quite exact because of the decomposition on melting).



To pure acetondicarbonicacid-diethylester prussic acid was added in statu nascendi; the cyanhydrine was saponified with strong sulphuric-acid, after dilution of the H<sub>2</sub>SO<sub>4</sub> with ice the diethylester of monoamide-citric acid was extracted with chloroform. This was purified by pressing between unglazed porcelain plates, dissolving in chloroform and precipitating with ligroine, until it had the required melting point and was colourless.

To a weighed quantity of this substance a small excess of normal sodium hydroxide solution was added; after 24 hours only the 2 estergroups were saponified as was proved by titration. The amide is very resistant to diluted solutions of sodium hydroxide at ordinary temperature<sup>2)</sup>.

Such a substituted citrate, in which one carboxylgroup has been made inactive, was compared with some acids with two carboxylgroups and one or more hydroxylgroups. As such were chosen:

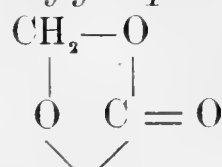


<sup>1)</sup> Lieb. Ann. **214**, p. 61—67.

<sup>2)</sup> SCHROETER, Berl. Ber. **38**, p. 3199.

Pure arabinose, prepared from arabinose was oxydised at 35° C for 24 hours with 2½ parts of nitric acid (spec. grav. 1,2). The superfluous HNO<sub>3</sub> was removed in the waterbath and the residue dissolved in 25 parts of water. This liquid was saturated at its boiling temperature with calciumcarbonate and filtrated while hot. The calciumsalt separated on cooling. The potassiumsalt was formed by adding the calculated quantity of potassiumcarbonate, decoloured with animal charcoal and purified by recrystallisation. As the calciumsalt is soluble only to a small extent, the acid could only be used in diluted dilution<sup>1)</sup>.

c. *The alcoholgroup and one carboxylgroup made inactive.*



The *methylencitric acid* COOH . CH<sub>2</sub> . C . CH<sub>2</sub> . COOH.

Methylencitric acid is formed by treating citric acid with formaldehyde and separating from the unchanged citric acid. I was presented with this substance in a very pure condition (as neutral sodiumsalt) freshly prepared by the Pharmaceutical Laboratory of the Elberfelder Farbenfabriken (Bayer)<sup>2)</sup>.

This compound was compared with some other dibasic acids without alcoholgroup:

*succinic acid* COOH.CH<sub>2</sub>.CH<sub>2</sub>.COOH.

*glutaric acid* COOH.CH<sub>2</sub>.CH<sub>2</sub>.CH<sub>2</sub>.COOH

*pimilinic acid* COOH.(CH<sub>2</sub>)<sub>3</sub>.COOH.

*suberic acid* COOH.(CH<sub>2</sub>)<sub>6</sub>.COOH.

d. *two or three carboxylgroups made inactive.*



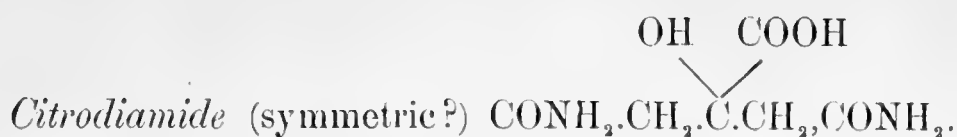
*Symmetric citric acid dimethylester* COOCH<sub>3</sub>.CH<sub>2</sub>.C.CH<sub>2</sub>.COOCH<sub>3</sub>,

100 gr. of citric acid were dissolved in 500 gr. methylalcohol and boiled for one hour after addition of 4 gr. H<sub>2</sub>SO<sub>4</sub>; this mixture was diluted with limewater, neutralized with CaCO<sub>3</sub> and filtered. The filtrate was concentrated in vacuo. After addition of HCl. the ester crystallized and was recrystallized from water. Melting-point (not very sharp) 125-127° C.<sup>3)</sup>.

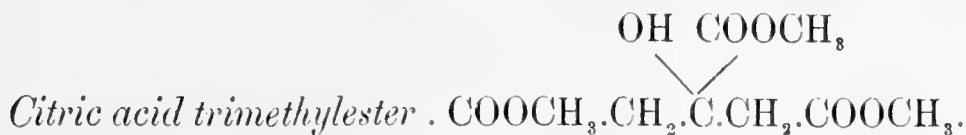
<sup>1)</sup> KILIANI, Berl. Ber. 21, p. 3007.

<sup>2)</sup> I am sincerely indebted to the Elberfelder Farbenfabriken for this kindness.

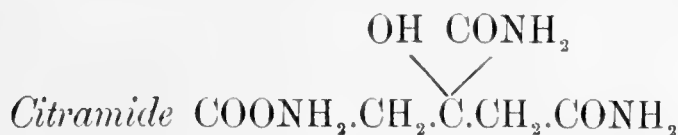
<sup>3)</sup> SCHROETER Berl. Ber. 35, p. 2086.



The motherliquor of the citramide (see below) was acidified with nitric acid and precipitated with alcohol. The citrodiamide is gained as a white crystalline powder<sup>1)</sup>. Usually the compound is mixed with its ammoniumsalt.

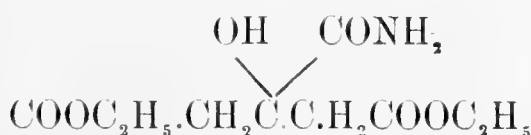


One part of citric acid was dissolved in one part of methyl alcohol and the solution saturated with HCl-gas. On cooling the ester crystallized and was purified by recrystallizing from methylalcohol. Purity controlled by melting-point.



Citric trimethylester was dissolved in 5 parts of strong ammonia (spec. grav. 0.88); soon the citramide precipitated and was recrystallized from water<sup>2)</sup>.

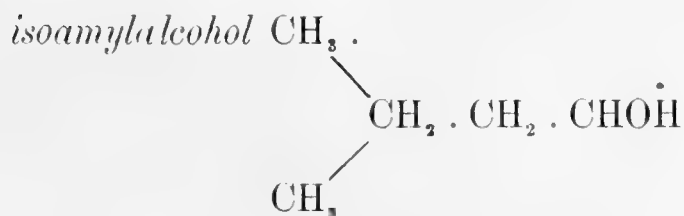
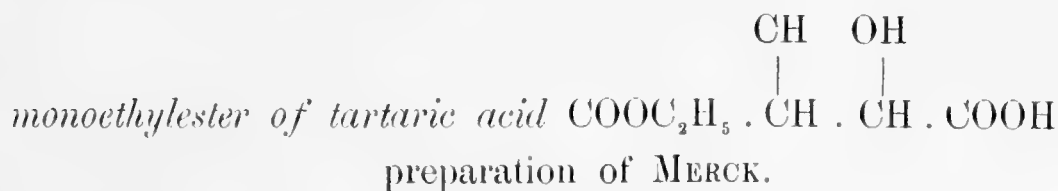
*Diethylester of monoamide-citric acid*



preparation described on page 437; purity controlled by melting-point.

The action of these substituted citrates was compared with the action of other organic compounds, having none or only one carboxyl group, but one or more hydroxylgroups.

We choose for comparison:



<sup>1)</sup> When no crystals of this substance are obtainable, it may last months before crystallization begins.

<sup>2)</sup> BEHRMANN und HOFMANN, Berl. Ber. 17, p. 2684.

<i>glycerine</i>	$\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CH}_2\text{OH}$
<i>erythrite</i>	$\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CH}_2\text{OH}$
<i>mannite</i>	$\text{CH}_2\text{OH} \cdot (\text{CHOH})_4 \cdot \text{CH}_2\text{OH}$
<i>glucose</i>	$\text{CH}_2\text{OH} \cdot (\text{CHOH})_4 \cdot \text{COH}$

*Influence of substituted citrates on curdling by rennet.*

It seemed natural to begin the investigation with that biochemical or pharmacological process, the nature of which seemed most simple and by which the smallest number of complicating circumstances might be expected.

To begin with, pharmacological actions may be excluded. For, an intravenously injected substance only acts after having been taken up by the tissues; the really acting concentration therefore is not only determined by the injected quantity (calculated pro kilogram of bodyweight) but also by the partition-coefficient tissue-blood, which is very different for different substances.

The same difficulty complicates the investigation of immunity reactions; here also the partition-coefficient leucocytes-serum or erythrocytes-serum varies considerably for various substances.

Remains the coagulation of blood and milk-curdling by rennet. Milkcurdling seems to be a so much simpler process than blood-curdling, the substances one has to work with, so much more stable, that milkcurdling seems to be the natural process to begin with. It is my intention to study later immunochemical and pharmacological processes with this method.

In order to find the influence of citrates on the curdling of milk, I first observed how much the curdling-time was lengthened after addition of increased quantities of neutral citrate of sodium. I prepared a  $\frac{1}{40}$  normal solution of sodiumcitrate, to which 2 drops of litmus-tincture were added and which by addition of a few drops of dilute hydrochloric acid or sodium hydroxide were brought to the same colour as distilled water with the same quantity of this indicator. 1  $\frac{1}{40}$  normal solution obtained in this way, was diluted to an  $\frac{1}{80}$  N,  $\frac{1}{100}$  N,  $\frac{1}{200}$  N,  $\frac{1}{500}$  N and  $\frac{1}{1000}$  N. I convinced myself that all these solutions remained neutral.

In order to determine the curdling-time, 10 cc. of raw milk were pipetted into a test-tube, 2 cc. of distilled water, resp. a solution of citrate of different strength, were added, the test-tube was closed with a cork or a stopper of cotton-wool, well mixed and placed in a waterbath of  $37^\circ$  C. until it had reached this temperature. Then 0.5 cc. of a solution of commercial rennet in distilled water (1 : 17)



was added with a pipet, the contents of the test-tube quickly reversed several times and again put into the waterbath. By carefully moving the test-tube from time to time, the moment when the milk became thicker, could be observed. When this change began, curdling was very near. The test-tube then was taken out of the waterbath and carefully inclined, so that some of the contents slowly moved along its walls, till at a certain moment floccules of about  $\frac{1}{2}$  m.m. suddenly appeared in the milk which adhered at its walls. This point was taken as the curdling-point. As milk-curdling is delayed by shaking and by cooling, care was taken to avoid all unnecessary movement and cooling. With some practise it is easy to reduce both factors to a minimum and then the curdling-time can be accurately determined. In the case of milk without citrate, the curdling-time seldom varied more than 15 seconds (in a curdling-time of  $2\frac{1}{4}$  minute); usually the observations differed less. After adding salts which only give a small delay, analogous differences were obtained; in the case of strongly delaying salts, the differences were somewhat larger, but always agreed sufficiently. Every curdling-time was determined in duplo or in triplo and the exact values found by taking the average. Curdling-times of more than 2 hours cannot be trusted because of the possibility of bacterial action.

It was found, that the kind of milk investigated on subsequent days with the same solution of rennet (1 : 17) gave curdling-times which varied little. In order to make observations on different days as well comparable as possible, the solution of rennet was always taken somewhat more or less diluted till a curdling-time of 2 minutes 18 seconds exactly was obtained, this being the value on the first day.

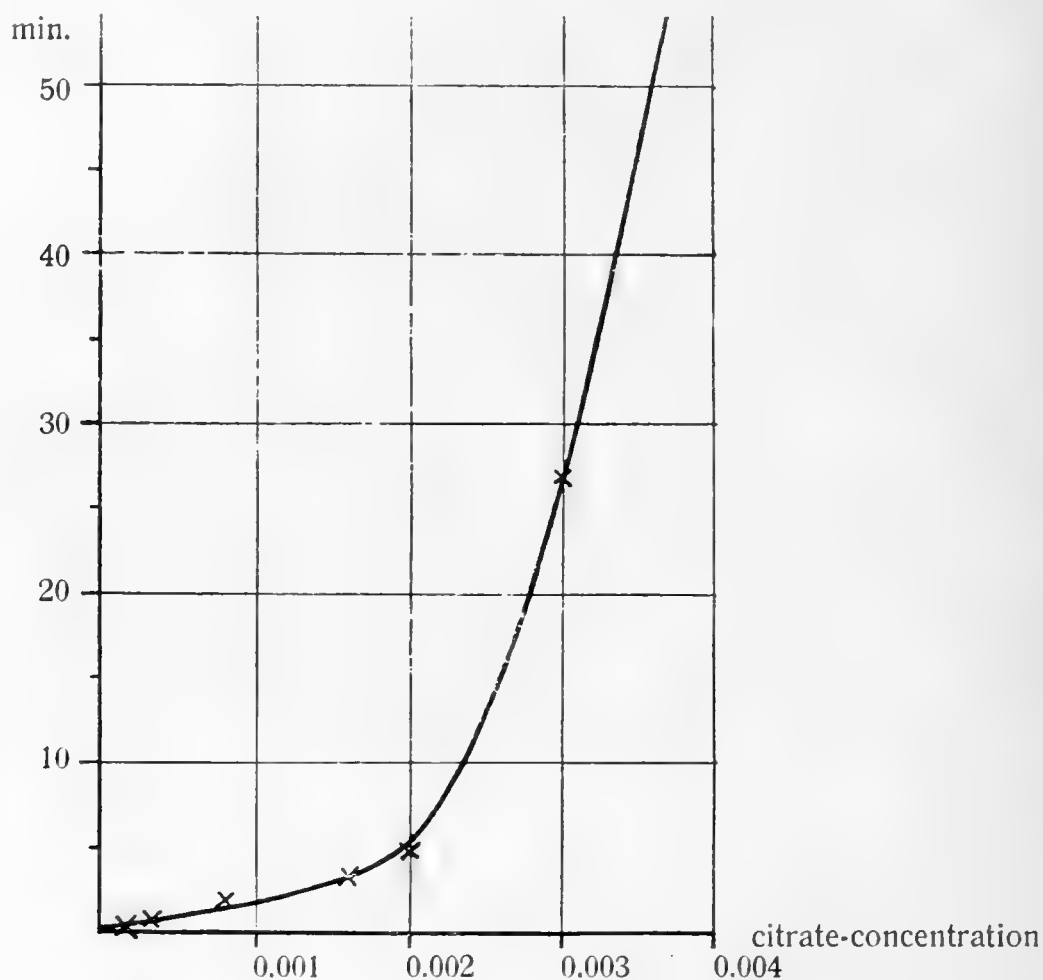
The lengthening of curdling-time found when the milk contained the quantities of citrate given below, is seen from the following figures :

0.00016 N	delay	17 seconds	0.0020 N	delay	289 seconds
0.00032 N	„	34 „	0.0030 N	„	27 min.(27')
0.0008 N	„	105 „	0.0040 N	„	84 „
0.0016 N	„	191 „	0.0080 N	„	9 hours.

These figures give the following curve (see p. 442).

Which is the best concentration to compare citrates with the substituted products? When the concentration is sufficiently large *all* salts inhibit milk-curdling. The characteristic of citrate-action is the fact that curdling is prevented in concentrations in which other salts give a scarcely perceptible delay. In general therefore the results of the comparative investigation will be the more correct,

the smaller the concentrations used. On the other hand the difficulty of accurately determining very small lengthenings of curdling-time,



forms another limit. The best concentrations proved to be  $1/125$  N and  $1/25$  N; citrates in this concentration practically inhibit milk-curdling, while indifferent salts as sodium chloride, sodium formiate among others show none or very little influence.

In order to find the influence of salt on milk-curdling,  $1/80$  gram-molecule <sup>1)</sup> of the acid was neutralized with titrated natron, with addition of two drops of litmustincture till the colour was the same as distilled water with the same quantity of indicator.

Then the volume was brought to 50 cc. with distilled water. In this way a neutral solution was obtained, containing  $1/4$  grammolecule of neutral salt per liter. In the same way or by diluting the  $1/4$  N. solution  $1/20$  N. solution of the neutral salts was obtained.

The curdling-time was determined as described above; only 2 c.c. of the salt was added instead of the 2 cc. of distilled water. After

<sup>1)</sup> Not  $1/80$  equivalent, but  $1/80$  molecule; therefore of a tribasical acid with mol. weight  $200 \frac{200}{80}$  gr. were dissolved.

all had been mixed and brought to the right temperature, again  $\frac{1}{2}$  cc. of diluted rennet was added. <sup>1)</sup>

I found the following lengthenings of curdling-time:

*a. The alcoholgroup made inactive.*

Acetylcitric acid  $\frac{1}{125}$  N  $3\frac{1}{2}'$   $\frac{1}{25}$  N  $9\frac{1}{2}'$

*compared with*

Aconitic acid  $\frac{1}{125}$  N  $2\frac{1}{2}'$   $\frac{1}{25}$  N  $9'$

Tricarballic acid  $\frac{1}{125}$  N  $2\frac{3}{4}'$   $\frac{1}{25}$  N  $9\frac{3}{4}'$

Isoallylentetracarboxylic acid  $\frac{1}{125}$  N  $3'$   $\frac{1}{25}$  N  $9\frac{1}{2}'$

*b. One Carboxylgroup made inactive.*

Symmetric citric acid-

monoamide  $\frac{1}{125}$  N  $1\frac{1}{4}'$   $\frac{1}{25}$  N  $6\frac{1}{2}'$

*compared with*

Malic acid  $\frac{1}{125}$  N  $1'$   $\frac{1}{25}$  N  $6'$

Tartaric acid  $\frac{1}{125}$  N  $1\frac{1}{4}'$   $\frac{1}{25}$  N  $6\frac{1}{4}'$

Trioxoglutaric acid  $\frac{1}{125}$  N  $1'$   $\frac{1}{25}$  N  $—$  <sup>2)</sup>

*c. The alcoholgroup and one carboxylgroup made inactive.*

Methylene citric acid  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $\frac{3}{4}'$

*compared with*

Succinic acid  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $1'$

Glutaric acid  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $1'$

Pimilinic acid  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $1\frac{1}{4}'$

Suberic acid  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $1\frac{1}{4}'$

*d. two or more carboxylgroups made inactive.*

Citric acid dimethylester  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $1\frac{1}{2}'$

Citrodiamide  $\frac{1}{125}$  N  $\frac{1}{4}'$   $\frac{1}{25}$  N  $1'$

Citric acid trimethylester  $\frac{1}{125}$  N  $-\frac{1}{4}'$   $\frac{1}{25}$  N  $—$  <sup>3)</sup>

Citramide  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $\frac{1}{2}'$

Diaethylester of the

citric acid-monoamide  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $\frac{1}{2}'$

*compared with:*

Monoethylester of

tartaric acid  $\frac{1}{125}$  N  $\frac{1}{4}'$   $\frac{1}{25}$  N  $1\frac{1}{4}'$

Isoamylalcohol  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $\frac{3}{4}'$

Glycerine  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $0'$

Erythrite  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $0'$

Mannite  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $— \frac{1}{4}'$

Glucose  $\frac{1}{125}$  N  $0'$   $\frac{1}{25}$  N  $0'$

<sup>1)</sup> I am indebted to Mr. ROSS VAN LENNEP for his valuable help in this part of the investigation.

<sup>2)</sup> Not examined because of the small solubility of the calciumsalt.

<sup>3)</sup> Not sufficiently soluble to be examined in this concentration.

When we consider that the unchanged citrate both in  $1/125$  and in  $1/25$  N solution delays the curdling more than 2 hours, it appears from the above table, that the action of citrate is very much weakened as soon as we substitute one of the active groups of the citric-acid-molecule, that it totally stops as soon as we make 2 or 3 groups inactive. In the case of tartaric salts we find the same influence of groups; when the alcoholgroups are made inactive (by acetylation) or one of the carboxylgroups (by esterification), the inhibiting action has disappeared (has fallen to the order of magnitude of all kinds of indifferent substances as is shown by the following figures).

When one group which is substituted, is an alcoholgroup, we get a delay of  $3\frac{1}{2}'$  with an  $1/125$  N and of  $9\frac{1}{2}'$  with  $1/25$  N. It seems very remarkable that the compared 3-basic acids without alcoholgroup give a delay of the same order of magnitude, viz.  $2\frac{1}{2}$ — $3'$  with  $1/125$  N and  $9\frac{1}{4}$ — $9\frac{3}{4}'$  with  $1/25$  N.

When the one group that has been substituted, is a carboxyl group, we get a delay of  $1\frac{1}{4}'$  with  $1/125$  N and of  $6\frac{1}{2}'$  with  $1/25$  N. while with the bibasic acids compared, with 2 carboxylgroups and 1 or more alcoholgroups, these figures are  $1$ — $1\frac{1}{4}'$  with  $1/125$  N and  $6$ — $6\frac{1}{4}'$  with  $1/25$  N. Here also we find a remarkable agreement.

When 2 or more of the active groups of the citrates are taken away, the lengthening of curdling-time diminishes to 0 à  $1/4'$  with  $1/125$  N and  $1/2$  à  $1\frac{1}{2}'$  with  $1/25$  N, figures which can be obtained also with the compared substances but are in the same order of magnitude as with various indifferent salts. It is therefore better to say, I think, that when 1 or more groups are taken away, the characteristic action of citrate has quite disappeared.

We can get a better insight into the relations here described, if we calculate what would be the concentration of citrate, necessary to give the same lengthening of curdling-time as a substituted citrate. For according to the figures on page 441 this lengthening increases much faster than in proportion to the concentration.

We find then that a lengthening of curdling-time

of $9\frac{1}{4}$ — $9\frac{1}{2}'$	corresponds with a citrate-concentration of	0.0023 N.
„ $6$ — $6\frac{1}{4}'$	„ „ „ „ „ „	„ 0.0021 N.
„ $1'$	„ „ „ „ „ „	„ 0.0003 N.

We can state therefore, that the characteristic citrate-action is diminished to about 6% of its original value, when one group has been taken away and is diminished to about 1%, when two groups are substituted. We have found, that an analogous influence on the curdling-time belongs to all salts which possess either three carboxyl-

groups and one or more alcoholgroups. It is the combination in one molecule of these two groups, which each delay curdling-time to a certain extent, which increases this power in the case of citrates so strongly (up to 16 times). It is remarkable that the alcoholgroup is as much necessary for the citrate action, as the carboxylgroups.

*Summer of 1911.*

*Delft, Hygienic Laboratory of  
the Technical University.*

**Biochemistry.** — "*The laws of surface-adsorption and the potential of molecular attraction.*" By J. R. KATZ. (Communicated by Prof. J. D. v. D. WAALS). (Introduction).

(Communicated in the meeting of June 1912).

*Exclusion of secondary complications.*

Surface-adsorption or adhesion plays an important part in biological and biochemical processes, but very little is known of its laws. Especially for the solving of some questions about swelling (imbibition) it is desirable to study this phenomenon more closely. Therefore I have made — although the subject really belongs more to physics than to biochemistry — some researches which are only intended as a first introduction to the study of this subject.

The confusion which is still reigning here, comes, I think, for a large part from the fact, that two different things again and again are mixed up: surface-adhesion at substances which have some other action on the adsorbed fluid (formation of a solid solution, swelling, formation of a chemical compound among others) and uncomplicated surface-adsorption. Among the authors who in the course of the 19th century have studied surface-adsorption, not a single one seems to have carried through this distinction as far as might be wished. And even the two latest investigators of this subject, TROUTON<sup>1)</sup> and FREUNDLICH<sup>2)</sup>, still treat the adsorption of water-vapour at glasswool and the adsorption at cotton- or woolfibres, as the same phenomenon; although glass does not take up water between its smallest particles, whereas wool and cotton do this to such an extent that the dimensions of the fibres become perceptibly larger (swelling).

Therefore I think it above all necessary in the experimental study of surface-adsorption, to choose a solid which has no action on the fluid studied. I choose water as the fluid to be investigated,

1) Proc. Roy Soc. 77 (1906) en 79 (1907).

2) Kapillarchemie.

because of the facility with which its vapour-tensions can be determined with the method to be explained below.

Dr. DAY, Director of the Geophysical Laboratory of the Carnegie Institution in Washington, who has great experience of silicates, advised me to begin with synthetical quartz and synthetical anorthite (Calciumaluminiumsilicate) as adsorbent solids, because these substances, when in mass, certainly do not take up water as a solid solution and have very little inclination to react chemically with water. Dr. DAY had the kindness to have both substances prepared for me in the most pure condition and to have them powdered in a motor-driven agate-mortar as finely as is possible. The material then was sieved through the finest metal sieve (80 meshes pro centimeter). In this way the surface of the solid was made as large as possibly can be attained; in this way the best chance was obtained that sufficiently large quantities of adsorbed fluid could be observed in the case of a solid substance which agrees as well as possible with the above requirement.

In order to get an impression how finely divided the substances were, I have suspended a weighed quantity in a known volume of water and have determined with the counting-apparatus for blood-corpuseles of Thoma, how many microscopically visible particles this suspension contained pro  $\text{m.m}^3$ . In this way it was found, that 1 mgr. of quartz contains 140 million particles and 1 mgr. of anorthite 120 million. Extraordinarily finely divided powders therefore!

I have determined for both substances the amount of water adsorbed as a function of the vapour-tension. Nine portions of this powder of 1 to 2 gr. each were carefully weighed in crystallizing dishes; these were treated as described below, in order to bring them in the same condition and then were placed above 9 different mixtures of sulphuric acid and water, of which the vapour-tension was known. There they remained until constant weight. Ignition in a porcelain crucible showed the amount of water contained in the material used. Controls showed, that the adsorption at the surfaces of the dishes was too small, compared with the adsorption at the surface of the powder, to have influence of importance.

*Influence of the preliminary treatment of the powder: the adsorbed layer consisting of vapour or of fluid.*

Theoretically there exist two possibilities, when a vapour condenses on the surface of a solid. Either it is condensed as vapour only, or the layer of fluid is formed on the solid.

That indeed different curves are obtained in the case of a solid which is covered with a thin layer of fluid or one by which this layer has been removed by intensive drying, is shown by the experiments of Trouton on the adsorption of water at glasswool<sup>1)</sup>. When the glasswool had been dried during 70 hours at 160° C. in vacuo over phosphorpentoxide (so that we may presume that the adhering waterlayer had been removed) curves were obtained as shown in the subjoined figure.<sup>2)</sup>

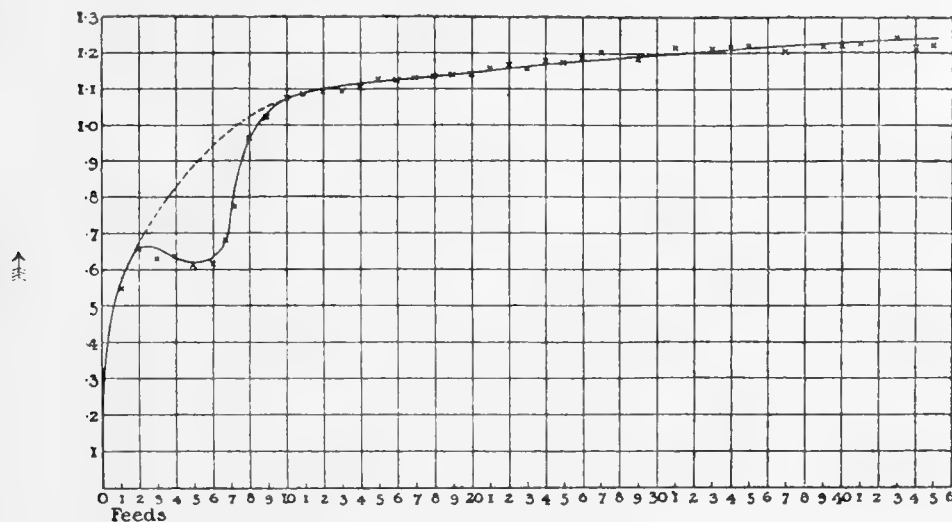


Fig. 1.

The abscissae represent the amounts of water (in arbitrary units) which are adsorbed at the surface of the glass, the ordinates represent the vapour-tension, which is in equilibrium with these. This curve was obtained when going from the driest towards the moister side. The curve rises quickly at the smaller values of the abscissae and turns its concavity downward, then shows a very curious maximum and minimum and finally quite continuously becomes a line, which in the main seems to agree with the line obtained when a layer of fluid water covers the surface of the glass.

TROUTON has realised this last case only in an impure form, probably because he had to meet the difficulty, that in his experimental technic the curves could only be followed from the driest to the moister side. As driest substance he used glasswool dried at room-temperature over phosphorpentoxide until the vapour-tension just had become zero. He then obtained the curve shown below.<sup>3)</sup>

<sup>1)</sup> Proc. Roy. Soc. **79**, p. 383—390.

<sup>2)</sup> l. c. p. 385.

<sup>3)</sup> l. c. p. 388.

This curve begins almost horizontally (the first one vertically!) and then has its *convexity* below; with larger abscissae it has its *concavity* below.

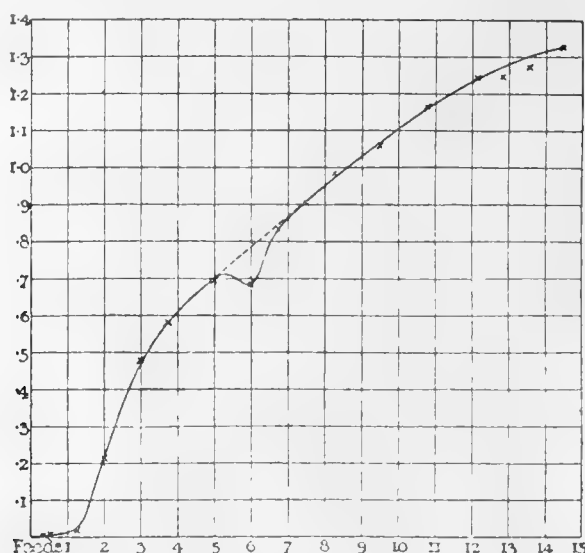


Fig. 2.

The curve still shows however something like a maximum and a minimum. Trouton ascribes this to the fact, that a part of the glasswool is really dry, which means in our conception that a part of it has lost its adherent layer of fluid water. Two different phenomena are thus measured together.

It would be very interesting to know how the curve would be in the other extreme case, viz. when it is certain, that all the glasswool is covered with a layer of fluid water, because, as we shall see, just in this case it can be predicted by approximate calculation how the shape of the curve will be.

#### *Description of my own experiments.*

In order to be sure, that a layer of fluid water covers the particles of the powder, weighed quantities of the powder were placed during several days in a bellglass above a 1% solution of sulphuric acid in water (vapour-tension  $\frac{99}{100}$  of the maximum tension of water)<sup>1)</sup>. Then the dishes were placed over the different mixtures of acid-water till they were of constant weight, in a room which (situated on the north and provided with double windows) had variations of temperature as small as possible.

The following was found as the relation between vapour-tension

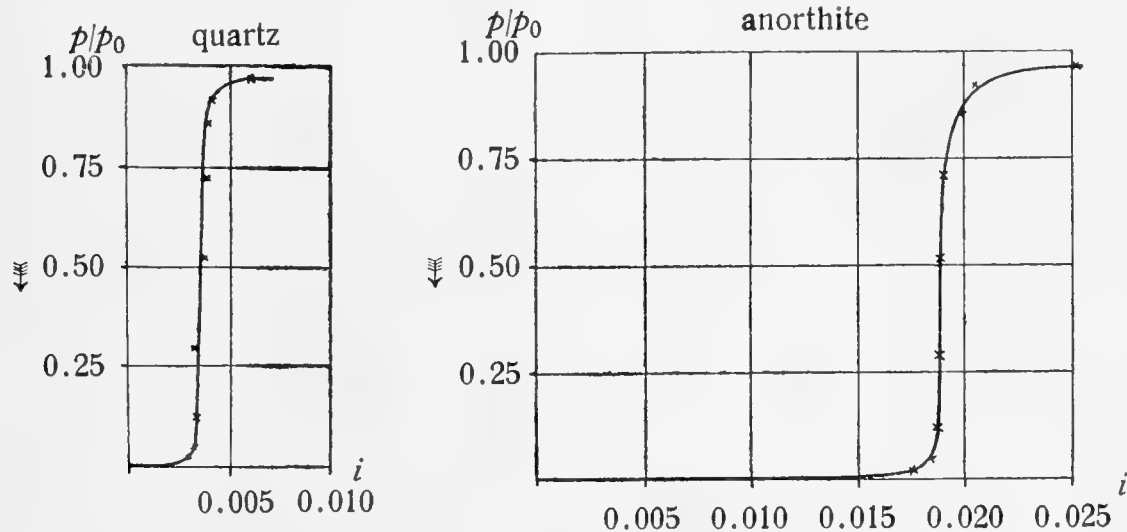
<sup>1)</sup> Pure water would have given too irregular condensations.



and quantity of adsorbed fluid ( $i$  being the quantity of gr. of water, absorbed by 1 gr. of dry powder).

QUARTZ		ANORTHITE	
$p/p_0$	$i \times 10^2$	$p/p_0$	$i \times 10^2$
0	0	0	0
0.020	0.29	0.020	1.79
0.048	0.31	0.048	1.85
0.122	0.33	0.122	1.87
0.306	0.34	0.306	1.88
0.525	0.39	0.525	1.89
0.718	0.40	0.718	1.91
0.857	0.41	0.857	1.99
0.915	0.42	0.915	2.04
0.965	0.61	0.965	2.53

By graphical representation the following curves were obtained:



Both curves begin with a more or less horizontal part, then have the convexity below, with larger  $i$  first have a flexible point, then have the concavity below; they therefore have the shape of an S.

*Thermodynamical relation between vapour tension and potential of molecular attraction.*

Prof. VAN DER WAALS now called my attention to the fact, that in the following manner an approximate theory of the shape of this

curve can be obtained. When a layer of fluid covers the surface and this is thick enough for us to assign to it the properties of fluid in mass, there exists a simple thermodynamical relation; at least when there is a discontinuous change in density of the layer of fluid and of the coexisting vapour (which is allowed as a first approximation) and when we neglect the very small compressibility of the water.

Then there exists for the vapour-tension  $p$ , coexisting with fluid water at a distance  $l$  from the solid wall, the relation:

$$RT \ln \frac{p}{p_0} = k$$

where  $k$  is the potential of the attraction of the solid wall on a distance  $l$ ,  $p_0$  the maximum-tension of water at the absolute temperature  $T$ , and  $R$  the constant of gases.<sup>1)</sup>

If the potential of molecular attraction were known, it would be possible to predict how the vapour-tension, which is in equilibrium with a layer of fluid of the thickness  $l$ , depends on  $l$ . And because the quantity of adsorbed water  $i$  (in gr. of water pro 1 gr. of dry powder) is related to the surface  $O$  according to the formula

$$l = \frac{i}{O}$$

it would be known at the same time, how the quantity of adsorbed water depends on the vapour-tension.

*The potential function of Lord RAYLEIGH and Prof. VAN DER WAAALS.*

Prof. VAN DER WAAALS proposed, that I should see how far we come with the potential function, which Lord RAYLEIGH and he had adopted in course of their studies about capillarity. They assumed

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<sup>1)</sup> This relation is easily deduced from the general property (VAN DER WAAALS—KOHNSTAMM, Lehrbuch der Thermodynamik I, p. 197) according to which in a system, subjected to the action of external forces, the *total potential* of a substance possesses the same value through the entire system. When  $\mu$  is the potential of water-vapour,  $\mu'$  the density-potential of water in the point  $l$  (that means the value which the potential of the water would have with the same density but without external forces) and  $k$  the potential of the molecular forces at a distance  $l$  at the solid wall, we have.

$$\mu' + k = \mu.$$

When the compressibility of water can be neglected,  $\mu = RT \ln p_0$ , while  $\mu = RT \ln p$ . It follows from this, that

$$k = RT \ln \frac{p}{p_0}.$$

that the potential on a distance  $l$  from a plain surface (pro unit of weight of adsorbed fluid) is represented by

$$k = -f e^{-\frac{l}{\lambda}}$$

where  $f$  is a large positive constant and  $\lambda$  is a number of the order of magnitude of the diameter of one molecule.

This leads to the relation.

$$RT \ln \frac{p}{p_0} = -f e^{-\frac{l}{\lambda}}$$

or

$$RT \ln \frac{p}{p_0} = -f e^{-\frac{i}{\sigma \lambda}}$$

Discussion of this function gives a curve which begins about horizontally, having its convexity below, then gets a point of inflection; with a still larger  $i$  it has its concavity downward, and finishes about horizontally. So exactly what has been found experimentally. On the relative values of the coefficients  $f$  and  $\lambda$  it depends how large the horizontal beginning will be. One could be in doubt for a moment, whether the formula deduced for a plain surface is valid for the particles of a powder. But as long as these particles are large, compared with the molecular dimensions, an error is made, which is not of importance. And how fine the powders of Dr. DAY may be, the diameter of the particles is always still large compared with the diameter of a molecule.

*Is it possible to determine from experiments on surface-adsorption how the potential function of molecular forces depends on distance?*

Finally an interesting question. We have seen, that the vapour-tension  $p$  and the potential of the molecular forces  $k$  (on a distance  $l$  from the glass-surface) are related to one another according to the formula

$$k = RT \ln \frac{p}{p_0}.$$

If the theory of Prof. VAN DER WAAALS is really a sufficient approximation, then it will be possible to calculate  $k$  from the measured vapour-tensions. So we get the relation between  $k$  and the adsorbed quantity of water  $i$ . We should like to know the manner in which

$k$  depends on distance. In order to calculate  $l$  from  $i$ , we must know the total surface of the powder. It is impossible to measure this accurately, but where an estimate is sufficient, we can try to calculate it from the number of particles pro mgr. as described on page 446.

We then assume, that the particles are spheres of equal dimensions and must know the specific gravity of the solids. In this way I have found for the surface of 1 gr.

quartzpowder	3260 cm <sup>2</sup>
anorthitepowder	3150 cm <sup>2</sup>

In this way I have found for the relation between potential and distance the following numbers ( $k$  expressed in cal. pro mol. adsorbed water)<sup>1)</sup>:

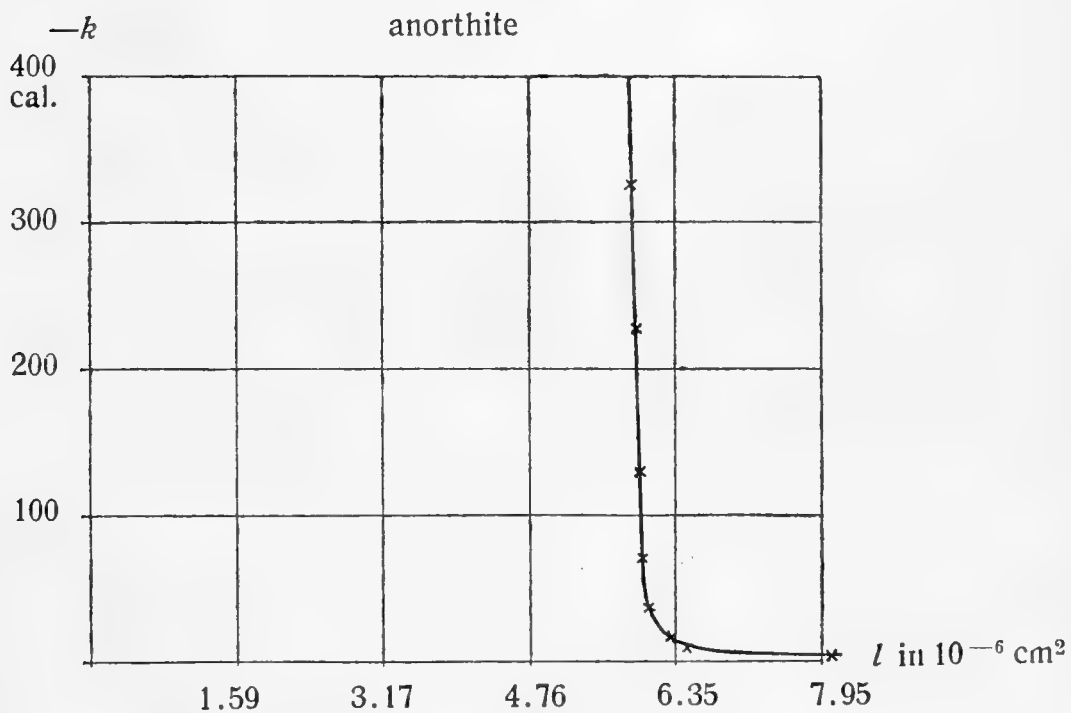
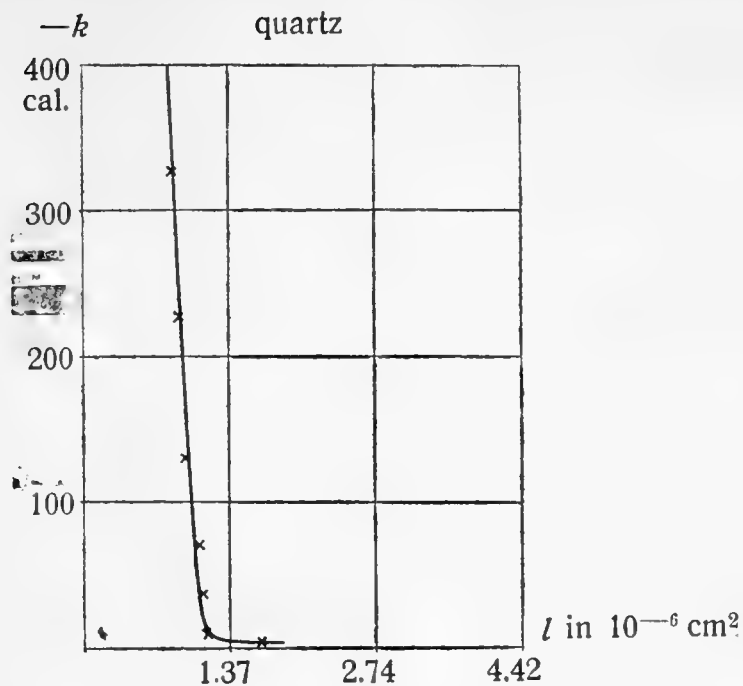
<i>water-quartz (Si O<sub>2</sub>)</i>			<i>water-anorthite (CaAl silicate)</i>		
$-k$	$i$	$l$ in 10 <sup>-6</sup> cm.	$-k$	$i$	$l$ in 10 <sup>-6</sup> cm.
328	0.0031	0.95	328	0.0185	5.87
228	0.0633	1.01	228	0.0187	5.94
128	0.0035	1.07	128	0.0188	5.97
69.8	0.0039	1.19	69.8	0.0189	6.00
36.0	0.0040	1.22	36.0	0.0191	6.06
16.7	0.0041	1.25	16.7	0.0199	6.32
9.62	0.0042	1.28	9.62	0.0204	6.48
3.86	0.0061	1.86	3.86	0.0253	8.03

These tables represented graphically, give the figures shown below; it is, I believe, the first time, that it has been tried to determine *experimentally* the form of the law of molecular attraction. Many assumptions are made about it in theoretical physics, but nobody has so far tried to determine its form by actual measurement. The *shape* of the curve obtained, is not dependent on the exactness of the estimate of the surface of the powder; an error in this estimate can only lengthen or shorten the figure in the direction of the abscissae.

It appears, that the potential diminishes rapidly with increasing distance and has a rather well defined "radius of the attraction-sphere"<sup>2)</sup>. For the size of this radius we find:

1) For 17° C.

2) We therefore come to the conclusion that the layer of fluid is almost in the whole course of the curve less thick than this radius. The supposition that the fluid has the properties of fluid in mass therefore only is exact as an approximation.



water-quartz  $1.3 \times 10^{-6}$  cm.

water-anorthite  $6.2 \times 10^{-6}$  cm.

while IHMORE<sup>1)</sup> has found in an analogous method (weighing with a very delicate balance the increase of weight of a plain surface of known size in a moist atmosphere)

water-brass  $0.27 \times 10^{-6}$  cm.

water-steel  $0.61 \times 10^{-6}$  cm.

water-nickel  $0.99 \times 10^{-6}$  cm.

water-rock-cristal 0.0 till  $6.0 \times 10^{-6}$  cm.

water-platina 0.0 „  $1.2 \times 10^{-6}$  cm.

water-Jenaglass 0.3 „  $4.0 \times 10^{-6}$  cm.

<sup>1)</sup> Wiedem. Arn. 31, p. 1006—1014. (1887).

Corresponding in order of magnitude with my figures.

There seems to exist no relation with the density of the solid. But it seems that substances with many atoms in the molecule have a larger radius.

Although the results found may still need correction from the fact, that the boundary of the waterlayer and the vapour is not so sharply defined as has been supposed, and because the compressibility of liquid water has been neglected, the results seem interesting enough to call attention to them. Perhaps then some one more competent on this subject, will deduce a less approximate theory. This theory will also have to answer the question, what is the relation between the maximum and the minimum in TROUTON'S curves with the maximum and the minimum in the isotherm of VAN DER WAALS, and if the supposition is right, that it is possible to calculate the maximum and the minimum of the equation of state from the minimum and maximum in TROUTON'S curves.

The importance of these investigations for the problem of swelling (imbibition) will be treated later.

**Meteorology.** — “*The Correlation between Atmospheric Pressure and Rainfall in the East-Indian Archipelago in connection with the 3,5 yearly barometric period*”. By Dr. C. BRAAK. (Communicated by Dr. VAN DER STOK).

(Communicated in the meeting of June 29, 1912).

The regularity of the East-Indian climate renders it eminently fit for clearly revealing weather variations of longer period. There the interest in the weather of next day is quite subordinate to the question whether the coming season will bring much or little rain and since predictions for the immediate future are not wanted, full attention can be paid to those for a more distant future. And this the more so as the circumstances there promise a much better chance of success for a prognosis of the seasons than elsewhere.

That the variations from one year to another are very considerable and an investigation of their character and origin is important, may, perhaps superfluously, be proved by the following summary: (p. 455)

One naturally looks for a relation between the oscillations in the rainfall and the barometric changes of long period.

These variations of the atmospheric pressure are of the same character over an area extending from British India over the Indian

## TOTAL RAINFALL IN M.M. IN THE MONTHS JULY, AUGUST, AND SEPTEMBER

Wet East monsoons				Dry East monsoons			
	Batavia	Ternate	Koepang		Batavia	Ternate	Koepang
1880	363	599	0	1881	121	268	0
82	144	485	36	83	30	254	0
89	148	475	4	85	22	61	0
90	290	452	18	88	34	42	1
92	248	353	1	91	102	321	0
95	262	470	44	96	51	393	0
98	162	402	10	1902	16	38	0
1900	146	370	82	05	119	261	22
04	340	145	16	11	155	133	0
06	364	434	3				
09	215	697	37				
10	258	305	5				
Average	245	432	21		72	197	3

Archipelago as far as Australia. They are regular and can with great approximation be represented by a series of waves with periods of 3 to 5 years; the other periods are quite subordinate. As a typical example we mention the atmospheric pressure at Port-Darwin where not only the amplitude is maximal, but also the variations are characterised by an extraordinary regularity<sup>1)</sup>. For this reason in what follows the rainfall in various parts of the Archipelago has been referred to the indications of the barometer at this station.

The stations whose observations are regularly published by the Batavia Observatory under the title "Rainfall observations in the Dutch East Indies" were arranged in groups, containing places of approximately similar situation. These contain from 1 to 5 stations and are:

1 North Sumatra, 2 North East Sumatra, 3 East Middle Sumatra, 4 Padang Highlands, 5 West Middle Sumatra, 6 South East Sumatra, 7 South West Sumatra, 8 West Borneo, 9 South Borneo, 10 North coast of West Java, 11 the Preanger district, 12 North coast of

<sup>1)</sup> Cf. Meteorologische Zeitschrift, Heft 1, 1912, p. 1.

Middle Java, 13 Madioen, Kediri, Blitar and Malang, 14 North coast of East Java, 15 the Lesser Sunda Islands and Timor, 16 West coast of South West Celebes, 17 East coast of South West Celebes, 18 South coast of North Celebes, 19 North coast of North Celebes, 20 Amahai, Banda, Ambon and Saparoea, 21 Wahai and Kajeli, 22 Ternate.

For our analysis the period 1883—1908 was chosen.

For each group the deviations of the monthly means were calculated from the monthly means of all the years of observation, including 1908. Since probably the oscillations in the rainfall have a retardation of about two months with respect to those of the atmospheric pressure<sup>1)</sup>, the barometric deviation for January, February etc. was always compared with the rainfall for March, April etc. Being only a small fraction of the total period, this shifting is indeed of secondary importance, but still it has the advantage of eliminating the pressure variations of short duration, which as a rule last a month or less and probably are not without any influence on the formation of rain.

In order to express mathematically the relation between rainfall and atmospheric pressure, the correlation factors between them were calculated for each group and for the twelve months. Denoting by  $x_1 x_2 x_3 \dots x_n$  the deviations of the separate monthly averages from the general monthly mean for the rainfall and by  $y_1 y_2 y_3 \dots y_n$  for the atmospheric pressure, the correlation factors are represented by<sup>2)</sup>:

$$r = \frac{\sum xy}{\sqrt{\sum x^2 \times \sum y^2}}.$$

The values of  $r$  have been collected in the following table.

From these data the following conclusions may be drawn:

*An influence of the mountain ranges on the correlation cannot be proved with certainty.* For the Preanger district behaves in the same way as the coast stations of Java and the stations of group 13, lying between high volcanoes. Also the West and East coast of South-West Celebes (except in January, February, March, and May), the South and North coast of North Celebes (except in April) and the stations to the North (group 21) and to the South (group 20) of the mountains of Ceram and Buru (except in February and April) behave generally in a similar way; besides, during

<sup>1)</sup> Cf. Natuurk. Tijdsch. voor Nederl. Indië, Vol. LXX, p. 110.

<sup>2)</sup> Cf. R. H. HOOKER: An elementary explanation of correlation . . . , Quarterly Journal Royal Met. Soc. Vol. 34, p. 277, 1908 and the extract by FELIX M. EXNER in Meteorol. Zeitschr. June 1910, p. 263.



## CORRELATION FACTORS

Atmosph. pressure at Port-Darwin — Rainfall in the Archipelago.

Group	Jan.	Febr.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
1	0.04	-0.10	-0.11	-0.00	0.07	0.14	0.22	-0.18	-0.09	0.16	0.10	0.07
2	.06	-.32	-.35	-.21	.05	.17	-.28	.09	.33	-.09	-.10	-.07
3	-.02	-.07	-.50	.45	.23	-.32	-.45	-.12	-.06	.13	.46	.19
4	.44	.42	-.15	.23	.09	.17	.06	-.26	.09	.12	.19	.03
5	.19	.29	-.10	.12	.38	.02	-.05	-.10	-.23	-.14	-.05	.01
6	.22	.01	-.30	.19	.05	-.12	-.12	-.29	-.23	-.52	-.61	-.17
7	-.15	.49	.03	-.04	.28	.19	-.32	-.43	-.31	-.53	-.25	-.14
8	.41	.25	-.06	.40	.19	.23	.02	-.29	-.30	.04	.00	.34
9	.16	.16	-.07	.46	-.03	-.03	-.29	-.27	-.33	-.25	-.25	-.05
10	.16	.01	.13	.40	.15	-.16	.00	-.20	-.28	-.45	-.06	.05
11	.34	.36	.05	.22	.07	-.19	-.03	-.19	-.25	-.44	-.38	-.03
12	-.08	-.05	.24	.00	-.32	-.16	.02	-.15	-.23	-.60	-.32	-.32
13	.37	.21	.31	.39	.01	-.06	.01	-.15	-.45	-.57	-.64	.38
14	.38	.12	.27	.11	-.35	-.30	.10	.09	-.20	-.41	-.69	-.12
15	-.04	-.11	.15	-.20	-.40	-.06	.12	.22	-.38	-.18	-.59	-.05
16	-.22	-.30	-.29	.22	.02	-.05	-.14	-.24	-.25	-.39	-.54	-.25
17	.35	.20	.42	.38	-.22	-.14	-.22	-.34	-.37	-.46	-.41	-.10
18	-.18	-.40	-.19	.30	.18	-.22	-.12	-.37	-.43	-.35	-.40	.30
19	-.46	-.22	-.37	-.04	.49	-.31	-.25	-.40	-.55	-.35	-.37	.18
20	.11	-.12	.32	-.33	-.50	-.38	-.33	-.54	-.36	-.18	-.37	-.35
21	.09	.48	.47	.42	-.36	-.27	-.30	-.37	-.28	-.23	-.55	-.24
22	-.35	-.37	-.40	-.28	-.00	-.38	-.33	-.39	-.37	-.37	-.53	-.26

the bracketed exceptional months the minus sign prevails on the South coast of South West Celebes and the plus sign on the East coast, while the stations of group 21, similarly situated with respect to the monsoons as the West coast, have the plus sign and those of group 20, situated like those on the East coast, the minus sign, which is exactly contrary to what one would expect if the mountains determined the sign.

On the other hand we clearly perceive a *variation of the correlation with the geographical longitude and latitude and with the season*. Leaving aside for the present the western part of the archipelago north of the equator, we find in the remaining part in the East monsoon with a few unimportant exceptions negative correlation, increasing in amount from West to East. In the West monsoon the negative sign still prevails in the East, in the West however the positive sign appears almost without exception, so that there a surplus of rain falls during the barometric maximum.

The explanation suggests itself that this change of sign of the correlation depends on the wind, which has also opposite directions in both monsoons. Now the relation between the barometric changes and the force of the monsoons is such that during the maximum of atmospheric pressure (caused by the relatively large amplitude of the barometric oscillation over Australia) the wind is reinforced during the East monsoon and weakened during the West monsoon, while at the minimum the opposite occurs <sup>1)</sup>. From this we conclude that *strengthening of the monsoon, either East or West, impedes the formation of rain*. This phenomenon must be partly ascribed to the development of fewer local showers when a stronger wind prevails, partly, especially in the East monsoon, but perhaps also in the West, to the circumstance that the air, when it moves in a quicker current, remains a shorter time above the sea.

The stronger negative correlation in the East would indicate that here, besides the influence mentioned above, still another factor makes itself felt, as well in the West as in the East monsoon. Very likely we have here a more direct influence of the neighbouring active centre in North Australia, *causing drought during the maximum by falling air-currents, rain during the minimum by rising currents*.

Though the variation of the correlation finds in this way a natural explanation for the greater part of the Archipelago, the matter is less simple for the remaining North-western part. There, as in Java, the correlation is, generally speaking, opposite for both monsoons, but it is negative when Java has a positive correlation and vice versa.

It is possible that the Barisan range, which in the northern part of Sumatra lies straight across the path of the monsoon, makes its influence felt. Also another explanation can however be given.

While during the maximum the influence of Australia increases the pressure difference in other places, it is quite possible that here

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<sup>1)</sup> Cf. *Natuurk. Tijdschrift voor Ned. Indië*, Vol. LXX, p. 105.

the opposite occurs. The difference namely of the barometric deviations at Batavia and Singapore changes in an irregular manner and points to a transitional region between these two places, whereas the difference between the deviations at Port-Blair (Andaman Islands), and those observed at Singapore, runs parallel with the barometric deviations at Port-Darwin, although with a small correlation ( $r=0,15$ ).

While the atmospheric pressure goes through its 3 to 5-yearly cycle, during the maximum in the South, Middle and East air-currents from the South would be superposed on the general flow of the monsoon and in the North-East, although to a smaller extent, from the North and currents from opposite directions during the minimum. Between the two currents a rising or falling movement should appear. The predominant positive correlation during the whole year in the Padang Highlands and in group 8 (Pontianak and Singkawang), which are approximately situated on the border line, might be a consequence of this vertical movement of the air. The correlation factors in the North-western exceptional region are small however, so that not much importance must be attached to these speculations.

Nor can we expect much for this region in the way of predictions, at any rate on the lines here developed. *Matters are quite different for the remaining part of the Archipelago, where the correlation undergoes regular changes and reaches fairly considerable values.*

The great question thus remains how we can obtain sufficient certainty about coming changes in the atmospheric pressure. Very likely we shall have to pay less attention than was done until now to the sun and the changes occurring there, but we shall have to look especially for a terrestrial cause and shall have to study the cooperation of meteorological phenomena over the whole world.

*For the temperature changes, observed in British India, the Archipelago and Australia find a natural explanation from the fluctuations in the general circulation of the atmosphere, accompanying the barometric changes, while it is difficult to bring them into relation with changes in the solar radiation, which surely would reveal themselves in a direct manner in temperature changes.*

These temperature changes are of a twofold nature:

1. In this tropical region, where long-period changes in the atmospheric pressure are brought about not dynamically, but entirely thermally, these must be accompanied by simultaneous temperature changes of opposite sign in the air-column above the spot of observation. In agreement with this we find e.g. from a comparison of the changes in atmospheric pressure at the mountain

station Kodaikanal (height 2340 m.) in the South of British India with those at the base-station Peryakalam (290 m.) that the average temperature of the intermediate layer undergoes oscillations of about  $0,7^{\circ}$  C., opposite to the simultaneous barometric changes at the base-station. The correlation factor between the two is  $r = 0,75$ . The station Kodaikanal evidently still lies in the stratum in which these temperature changes occur, for the temperature there changes in the same way as in the layer underneath. The correlation factor between the two temperature changes is  $r = 0,69$ .

With an amplitude of the atmospheric oscillation of 0,6 mm. at sea-level and of the temperature oscillation of  $0,7^{\circ}$  C., the air-stratum in which both changes would be in harmony would lie at about 1000 m. above the mountain station. The temperature changes are in this case restricted to the *condensation level*.

The results of ELIOT's investigations <sup>1)</sup> would show that this is a general phenomenon. From a comparison of the barometric changes at the mountain stations in British India with those of the stations in the plains, he deduced that during the barometric maxima at sea-level, an abnormally large quantity of air is found below the level of the mountain stations and an abnormally small quantity during the minima. The temperature changes that determine the barometric pressure here occur in the lower 2000 tot 3000 metres in the region where the heat of condensation plays an important part.

2. In the very lowest strata of the atmosphere the oscillation of the temperature is of a different nature. Over the whole of the area here considered the temperature of the stations in the plains follows namely very regularly the identical barometric change with a lag of about six months <sup>2)</sup>. This oscillation of the temperature must have had a disturbing action on the observed barometric oscillation, since the phase differs by about a year (i.e. more than  $\frac{1}{4}$  period) from the value required for the formation of the barometric oscillation (see 1). Still no disturbance is observed and the curves representing the barometric oscillation and these temperature changes generally show great similarity. This must probably be ascribed to the small thickness of this layer, which consequently has to be considered as a thin transition layer resting on the surface of the earth.

The temperature oscillations mentioned sub 1 and 2 are in complete agreement with the following scheme of changes :

If we suppose the general circulation of the air to be subjected to fluctuations in such a way that it is increased by the barometric

<sup>1)</sup> Indian Metereological Memoirs VI, p. 102.

<sup>2)</sup> Cf. Metereol. Zeitschrift loc. cit.

minimum in India and Australia and weakened by the maximum, as must undoubtedly be the case, the successive stages may be imagined as follows. During the barometric minimum an increased mixing takes place with the cool air from higher latitude together with an increased supply of cold water. By these causes after the barometric minimum a temperature minimum is developed in the lower strata of the atmosphere. In the upper strata, however, by the greater heat of condensation, resulting from the increased ascending motion of the air, a temperature maximum will develop simultaneously with the barometric minimum and this maximum will in its turn determine and strengthen the barometric minimum. This latter process will continue until the progressive sinking of the temperature of the water and the air below, cause the condensation to diminish and the atmospheric pressure to rise by a smaller supply of water-vapour and greater density of the air and in this way the following phase is prepared.

The energy required for keeping up this process is partly supplied by the increased heat of condensation during the barometric minimum and may for another part be derived from the interaction with the active centres of higher latitude where the deviations, once started, reinforce themselves, contrary to the tropical system of circulation where they are self-regulating<sup>1</sup>).

*Weltevreden*, May 10, 1912.

**Geology.** -- "*On Orbitoids of Sumba*". By Dr. L. RUTTEN. (Communicated by Prof. A. WICHMANN).

(Communicated of the meeting of September 28, 1912).

From Professor WICHMANN I received a short time ago a small collection of specimens of rocks and fossils belonging to a collection gathered by Mr. H. WITKAMP, geologist of the Bataafsche Petroleum-Maatschappij in the southern part of the Island of Sumba.

I beg to communicate here some particulars about the Orbitoids found in this collection. In 5 of the samples sent to me I discovered Orbitoids i.e. in 4 numbers (81, 114, 166 and 167) the subgenus *Orthophragmina*, and in 1 number (105) the subgenus *Lepidocyclina*.

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<sup>1</sup>) Cf. *Metereol. Zeitschr.* loc. cit.

*Orthophragmina.**Previous findings in the Dutch East Indies.*

The first *Orthophragmina* were described by R. D. M. VERBEEK<sup>1)</sup> from South-East Borneo. A few years afterwards his material was investigated by VON FRITSCH<sup>2)</sup>, who determined 5 species. A short time after K. MARTIN<sup>3)</sup> reported the existence of Orbitoids with Nummulites of the river Teweh in South Borneo, whilst TH. POSEWITZ had collected in the neighbourhood of Muara Teweh analogous *Orthophragmina* as VERBEEK had gathered in South-East Borneo<sup>4)</sup>.

In recent times H. DOUVILLÉ<sup>5)</sup> and IRENE PROVALE<sup>6)</sup> have again described *Orthophragmina* of South Borneo whilst the latter determined moreover a series of *Orthophragmina* of Udju Halang on the Upper-Makaham (Central Borneo)<sup>7)</sup>.

Of West Borneo we know through JENNINGS<sup>8)</sup>, and R. B. NEWTON and R. HOLLAND<sup>9)</sup> some findingplaces of *Orthophragmina*.

In Java Orbitoides with rectangular median chambers have been found at the surface in the residences of Bagelen, of Djokjokarta and of the Preanger<sup>10)</sup> Regencies, whilst also in a boring near Ngembak (Recidency of Samarang) a few *Orthophragmina* were found<sup>11)</sup>.

1) R. D. M. VERBEEK. Die Nummuliten des Borneo-Kalksteines. Neues Jahrbuch für Mineralogie etc. 1871, p p. 1—11.

2) K. v. FRITSCH. Einige eocäne Foraminiferen von Borneo. Jaarboek van het Mijnwezen in Ned.-Indië. 1879. 1. p.p. 236—251.

3) K. MARTIN. Neue Fundpunkte von Tertiärgesteinen im Indischen Archipel. Samml. Geol. Reichsmuseums. Leiden. (1). 1. 1881—83, p.p. 131—193.

4) TH. POSEWITZ. Das tertiäre Hügelland bei Teweh. Nat. Tijdschr. van Ned.-Indië XLIII. 1884, p p. 169—175. — TH. POSEWITZ. Borneo. 1889. p.p. 383—384.

5) H. DOUVILLÉ. Les Foraminifères dans le tertiaire de Bornéo. Bull. Soc. géol. de France. (4). 5. 1905, p.p. 435—464.

6) I. PROVALE. Rivista italiana di Paleontologia. 15. 1909. p.p. 65—96.

7) I. PROVALE. Rivista italiana di Paleontologia. 14. Perugia 1908, p.p. 55—80.

8) A. V. JENNINGS. Geological Magazine (3). 5. 1888. p p. 530—532.

9) R. B. NEWTON and P. HOLLAND. Annals and Magazine of Natural History. (7). 3. 1899, p.p. 245—264.

10) R. D. M. VERBEEK. Tijdschr. Ned. Aardr. Genootschap. 1, Amsterdam 1876, p.p. 291 et seq.

K. MARTIN. Samml. Geol. Reichsmuseums. Leiden. (1). 1. 1881—83. p.p. 105—130.

R. D. M. VERBEEK. Natuurkundig Tijdschrift van Nederl.-Indië. 51. 1892. p.p. 101—138.

R. D. M. VERBEEK et R. FENNEMA. Description géologique de Java et Madoura. 1896. Tome 2.

C. SCHLUMBERGER. Bull. Soc. géol. de France. (4). 3. 1903. p.p. 293 et seq.

H. DOUVILLÉ. Samml. des Geol. Reichsmus. Leiden. (1). 8. 1904—12. p.p. 279—294.

11) K. MARTIN. Samml. des Geol. Reichsmus. Leiden. (1). 3. 1887. p.p. 327 et seq.

For a short time past *Orthophragmina* of Nias<sup>1)</sup> are known, whilst in the eastern part of our archipelago they were found in West Celebes<sup>2)</sup>, West Timor, the new island near Ut, Great Kei, Kilwair, Tofuré, in New-Guinea eastward of the Etna Bay, Rendjuwa<sup>3)</sup> and in West Buru<sup>4)</sup>.

With the great number of very often incompletely described species of *Orthophragmina* that are known from the Dutch East-Indies, it will often be difficult to decide with which species a special form must be classed; fortunately this difficulty did not present itself with regard to the Sumba material, as the *Orthophragmina* in question belong to 2 wellknown species, *O. javana* Verb. and *O. dispansa* Sow., as will appear from the description.

*Orthophragmina javana* VERBEEK.

- Syn. *O. papyracea* Boubée, in von Fritsch 1879?  
*O. papyracea* Boubée, var. *javana* in Verbeek. T. A. G. 1.  
*O. papyracea* Boubée, var. *javana* in Verbeek 1892 and 1896.  
*O. dispansa* Sow. in Martin 1881 (partim).  
*O. javana* Verbeek in Douvillé 1905.  
*O. javana* Verbeek in Douvillé 1912.  
*Discocyclina discus* Rüttimeyer in Verbeek 1908. p. 304.

From the finding-place n<sup>o</sup>. 105 I received 5 isolated *Orthophragmina*, which, though they are very different in size (diam. 6, 12, 14, 24 and 27 mm.), cannot be separated from one another and must be classed with one species.

The pretty well conserved fossils have the form of regular lenses, showing either no central chamber at all or one which is but little pronounced in its youth; most of them are symmetrically thickened towards the centrum; the specimen of 27 mm. diameter had a thickness of 6 mm. The surface of the fossils is somewhat disintegrated, so that the fine-granular, dense, and very symmetrical granulation cannot very well be seen. Three horizontal sections were made, from which it appeared that the larger specimens of 24 and 27 mm. diameter were microspheric and the one of 12 mm.

<sup>1)</sup> H. DOUVILLÉ. Samml. des Geol. Reichsmuseums Leiden. (1). 8. 1904—12. p.p. 253—278.

<sup>2)</sup> H. DOUVILLÉ. l.c. 1905.

R. D. M. VERBEEK. Molukkenverslag. Jaarb. van het Mijnw. Wetensch. Ged. XXXVII. 1908, p.p. 54, 80, 81.

<sup>3)</sup> R. D. M. VERBEEK. l.c. 1908. p.p. 398, 625, 613, 616, 255, 474, 754 en 304.

<sup>4)</sup> J. WANNER. Centralbl. für Mineralogie, Geologie und Paläontologie. 1910, p. 140.

diameter was megalospheric. With regard to the two first-mentioned specimens I did not succeed in including the little embryonal chamber into the preparation.

### 1. Megalospheric form.

The median plane is but little curved: the median chambers form frequently incomplete circles round the very large embryonal chambers, whose maximal and minimal diameters are  $2500\ \mu$  and  $1800\ \mu$ . The parietis of the embryonal chamber is thin. The peripheral, median chambers of the first round are larger than those situated more outward:

1<sup>st</sup> round diameter of the chamber radiary  $190\ \mu$ , tangentially  $55-75\ \mu$   
more peripherically maxim. diameter radiary  $150\ \mu$ , tangentially  $60\ \mu$ .

### 2. Microspheric form.

In these large Orbitoids of exterior regular lensshape the median plane shows a strong saddle-shaped curve, as in the median horizontal section only narrow ligaments of median chambers running hyperbolically have been struck (comp. VERBEEK and FENNEMA 1896. Pl. 10, Fig. 150). The radiary diameter of the median chambers increases from the centre of the periphery, though constantly smaller chambers are scattered among the larger ones. The normal dimensions of the chambers are about:

At 2 mm. from the centre: radiary  $45-75\ \mu$ , tangentially  $35-55\ \mu$ .

Nearer to the periphery: ,,  $135-190\ \mu$ , ,,  $35-55\ \mu$ .

The grouping of the intermediate skeleton-columns to which of late, for a systematical purpose, DOUVILLÉ (l. c, 1912) attaches such a great value can distinctly be observed. Their thickness in tangential diameter is  $55-95\ \mu$ , it may be however that very near the periphery they are a little thicker. As a rule columns are only separated from each other by a single row of spacious lateral chambers.

Consequently the exterior habitus and structure of these Formanifera correspond very well with the forms described by VERBEEK (1896) as *O. papyracea* var. *javana* and with those described by DOUVILLÉ (1912) as *O. javana*, only the megalospheric form of this species was not yet known hitherto.

From the finding-place near Mount Madu (n<sup>o</sup>. 81) I received two Orbitoids (diam. 14 and 30 mm.) which correspond very well with the former, and the larger of which was again microspheric. I succeeded in including into the preparation the very small embryonal chambers round which the first peripheral cham-



bers are grouped in circles. The tangential diameter of these first rounds of peripheric chambers is larger than the radiary one (comp. VERBEEK 1896, pl. 10 f. 157). The columns are here a little thicker (100—180  $\mu$ ) than with the forms described above; they show both in a transversal and in a longitudinal section a very distinct, fibrous structure. The lumen of the lateral chambers is in a vertical direction very wide and their horizontal parietes are very thin.

From the finding-place N<sup>o</sup>. 167 *a* I received likewise a specimen of *O. javana*.

*Orthophragmina dispansa Sowerby.*

Syn. *O. dispansa* Sow. in VON FRITSCH 1879?

*O. dispansa* Sow. in VERBEEK 1892 and 1896.

*O. dispansa* Sow. in MARTIN 1881 (partim) and 1887.

*O. dispansa* Sow. in DOUVILLÉ 1912.

The rock N<sup>o</sup>. 16 is entirely filled up with Orbitoids which, by disintegration, are partly laid bare, so that their exterior habitus can be studied. The maximal diameter amounts to 9 mm, the height to 3 mm. The fossils are considerably thickened in the centre, whilst at the periphery they have an excessively thin edge. The surface is strongly granulated; the granulae however are not symmetrically divided over the whole surface. They are largest on the central tubercle (100—190 $\mu$ ), towards the periphery they become very small, but on the very thin edge again larger granulae are perceptible.

Though in general the granulae are separated by a single row of spacious lateral chambers, it often occurs that there are two rows of chambers between them.

In sections only macrospheric individuals were found. The diminutive size and the spacious lateral chambers make this form correspond entirely to *O. dispansa* Sow, as DOUVILLÉ described them a short time ago (1912).

Rare specimens of Calcarina and little Nummulites are found in the limestone N<sup>o</sup>. 238, together with these Orthophragmina, whilst it is by no means impossible that still another very thin Orthophragmina is met with: the material was however insufficient to decide in this respect.

*Lepidocyclina.*

The brecciated rock N<sup>o</sup>. 105 contains many but fragmentary fossils, among which Lithothamnium, Cycloclypeus, Heterostegina, and Lepidocyclina can be recognized.

The individuals of the latter genus seem to reach a size of about 10 mm.; the median chambers are spatulated to rhombic. It is impossible specifically to determine them for want of orientated sections, and isolated specimens.

Since VERBEEK's publication of 1892, nearly all authors on Indian Orbitoids agree that Lepidocyclina and Orthophragmina never occur together in one stratum, and that the latter are characteristic of the Eocene, the former of the Upper-Oligocene and Miocene.

J. PROVALE (l. c. 1908) holds a different view, she describes Orthophragmina and Lepidocyclina of Udju Halang in Central Borneo, which are said to proceed from one stratum, whilst G. OSIMO<sup>1)</sup> has mentioned rare Lepidocyclina of West Celebes (Donggala) that are reported to occur with eocene Nummulites. These assertions should, however, be accepted with some reserve.

In the first place at Udju Halang Lepidocyclina and Orthophragmina are not found in one and the same rock (PROVALE l. c. 1909 p. 75)<sup>2)</sup>, so that it is likely that they occur in the proximity of each other, but not in the same stratum.

The same possibility, however, exists for the findingplaces near Donggala, the more so as VERBEEK (l. c. 1908, p.p. 58, 59) ascertained for the surroundings of Pangkadjéné and Maros, northward from Makassar the existence of eocene limestone with Orthophragmina, and of oligo-miocene limestone with Lepidocyclina the one in the proximity of the other.

For the present we may consequently certainly stick to the old view that in India Orthophragmina characterizes Eocene, Lepidocyclina on the other hand the Upper-Oligocene, so that from the above we may make the conclusion that in Sumba both Eocene and Miocene must be found. The limestone and marls of Sumba that are known up to the present (VERBEEK l. c. 1908) originated from the northern part of the island and were usually very young; the older ones were most likely classed with Miocene.

*Buitenzorg, August 1912.*

1) G. OSIMO. *Rivista italiana di Paleontologia*, 14 Perugia 1908, p.p. 21—54.

2) I. PROVALE indicates in this place the age of the Orthophragmina as eocene, that of the Lepidocyclina as oligocene. (?)



spacial representation on the side plane  $\text{KCl}-\text{BaCl}_2-\text{CuCl}_2$  of the tetrahedron which projection may be easily deduced in the well known manner from the representation in space<sup>1)</sup>.

Fig. 1 gives a schematic representation of the equilibria occurring at  $40^\circ$ .

The equilibria occurring in the ternary system  $\text{BaCl}_2-\text{CuCl}_2-\text{Water}$  are represented by the curves  $ab$  and  $bc$  situated on the side plane  $\text{BaCl}_2-\text{CuCl}_2-\text{Water}$ .

$ab$  is the saturation line of the  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

$bc$  „ „ „ „ „  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

The solution  $b$  is saturated with both salts.

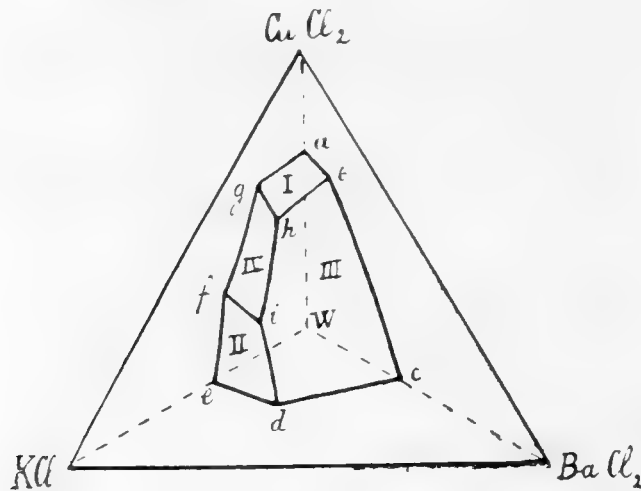


Fig. 1.

The equilibria occurring in the ternary system:  $\text{KCl}-\text{BaCl}_2-\text{Water}$  are represented by the curves  $cd$  and  $de$  situated on the side plane:  $\text{KCl}-\text{BaCl}_2-\text{Water}$ .

$cd$  is the saturation line of the  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

$de$  „ „ „ „ „  $\text{KCl}$ .

The solution  $d$  is saturated with both salts.

The curves  $ef$ ,  $fg$  and  $ga$  situated on the side plane  $\text{KCl}-\text{CuCl}_2-\text{Water}$  represent the equilibria in the ternary system  $\text{KCl}-\text{CuCl}_2-\text{Water}$ .

$ef$  is the saturation line of the  $\text{KCl}$ .

$fg$  „ „ „ „ „  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .

$ga$  „ „ „ „ „  $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$ .

Hence the solubility line of the double salt  $\text{D}_{1.2.2} = \text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$  is limited in point  $f$  by the occurrence of solid  $\text{KCl}$  and in point  $g$  by the occurrence of solid  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .

<sup>1)</sup> Z. f. Phys. Chem. **65**, 563 (1909).

In the quaternary system occur solutions saturated with one, two and three solid substances.

Those saturated with one solid substance only are represented by a plane, the saturation plane of that substance.

Plane I or  $abhg$  is the saturation plane of the  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .  
 „ II „  $edif$  „ „ „ „ „ „ „  $\text{KCl}$ .  
 „ III „  $cbhid$  „ „ „ „ „ „ „  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .  
 „ IV „  $fghi$  „ „ „ „ „ „ „  $\text{D}_{1.2.2}$ .

The intersecting lines of these saturation planes indicate the solutions saturated with two solid substances; thus we find:

Curve  $bh$  is the saturation curve of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .  
 „  $di$  „ „ „ „ „ „ „  $\text{KCl} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .  
 „  $fi$  „ „ „ „ „ „ „  $\text{KCl} + \text{D}_{1.2.2}$ .  
 „  $ih$  „ „ „ „ „ „ „  $\text{D}_{1.2.2} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .  
 „  $hg$  „ „ „ „ „ „ „  $\text{D}_{1.2.2} + \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .

The solutions saturated with three solid substances are represented by the points of intersection of the saturation planes;

Point  $h$  is the saturation point of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O} + \text{D}_{1.2.2}$ .  
 „  $i$  „ „ „ „ „ „  $\text{KCl} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O} + \text{D}_{1.2.2}$ .

If we remember that the equilibria represented in Fig. 1 apply only to one definite temperature  $T$  and to one definite pressure  $P$ , we notice occurrence of the following equilibria:

A. Invariant ( $P, T$ ) equilibria ( $n$  Components in  $n$  phases)

1. binary: the point  $a, c$  and  $e$ ;
2. ternary: „ „ „  $b, d, f$  and  $g$ ;
3. quaternary: „ „ „  $i$  and  $h$ .

B. Monovariant ( $P, T$ ) equilibria ( $n$  Components in  $n-1$  phases)

1. ternary: the Curves  $ab, bc, cd, de, ef, fg$  and  $ga$ .
2. quaternary: the Curves  $bh, hi, id, if$  and  $gh$ .

C. Divariant ( $P, T$ ) equilibria ( $n$  Components in  $n-2$  phases.

1. quaternary: the planes I, II, III and IV.

The equilibria occurring at  $60^\circ$  are represented schematically in fig. 2; this is distinguished from fig. 1 in so far that between the saturation plane I and IV of fig. 1 another saturation plane V has introduced itself so that the following saturation planes occur.

Plane I, or  $ablk$ , the saturation plane of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$   
 „ II „  $edif$ , „ „ „ „ „ „ „  $\text{KCl}$   
 „ III „  $cbhid$ , „ „ „ „ „ „ „  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$   
 „ IV „  $fghi$ , „ „ „ „ „ „ „  $\text{D}_{1.2.2}$   
 „ V „  $ghlk$  „ „ „ „ „ „ „  $\text{D}_{1.1}$

If we compare the figs 1 and 2 we notice that the equilibria in the two ternary systems  $\text{CuCl}_2\text{—BaCl}_2\text{—Water}$  and  $\text{KCl—BaCl}_2\text{—Water}$ , do not show appreciable differences at  $40^\circ$  and  $60^\circ$ , but that these are observed in the ternary system  $\text{CuCl}_2\text{—KCl—Water}$  and in the quaternary system.

At  $40^\circ$  (Fig. 1) the isotherm of the ternary system  $\text{KCl—CuCl}_2\text{—H}_2\text{O}$  consists of:

$ef$ , the saturation line of the  $\text{KCl}$   
 $fg$ , „ „ „ „ „  $\text{D}_{1.2.2}$   
 and  $ga$ , „ „ „ „ „  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

whereas this consists at  $60^\circ$ , (Fig. 2), of:

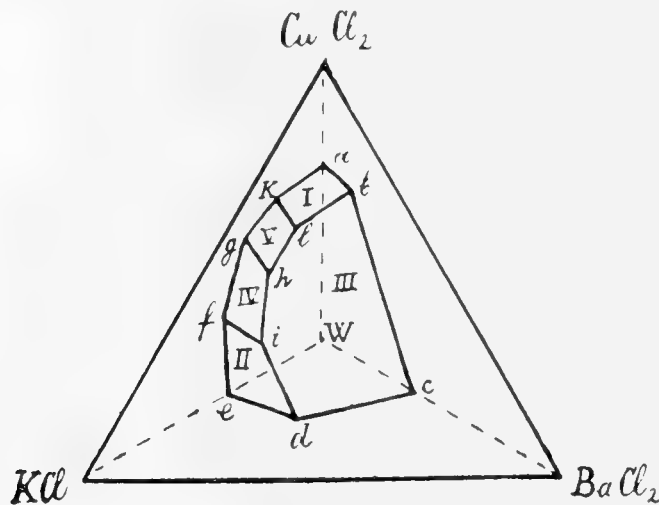


Fig. 2.

$ef$ , the saturation line of the  $\text{KCl}$   
 $fg$ , „ „ „ „ „  $\text{D}_{1.2.2}$   
 $gk$ , „ „ „ „ „  $\text{D}_{1.1}$   
 and  $ka$ , „ „ „ „ „  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

Whereas at  $40^\circ$  only 5 quaternary saturation curves occur, seven are found at  $60^\circ$ , namely.

Curve  $bl$ , the saturation curve of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$   
 „  $di$ , „ „ „ „  $\text{KCl} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$   
 „  $fi$ , „ „ „ „  $\text{KCl} + \text{D}_{1.2.2}$   
 „  $hi$ , „ „ „ „  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O} + \text{D}_{1.2.2}$   
 „  $hg$ , „ „ „ „  $\text{D}_{1.2.2} + \text{D}_{1.1}$   
 „  $hl$ , „ „ „ „  $\text{D}_{1.1} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$   
 „  $kl$ , „ „ „ „  $\text{D}_{1.1} + \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .

The saturation curve  $gh$  of fig. 1 (at  $40^\circ$ ) is, therefore replaced in fig. 2 (at  $60^\circ$ ) by the three saturation curves  $gh$ ,  $hl$  and  $lk$ .

At  $40^\circ$  (fig. 1) we find only two, at  $60^\circ$  (fig. 2) however, three quaternary saturation points, namely:

Point *i*, the saturation point of  $\text{KCl} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O} + \text{D}_{1.2.2}$

„ *h*, „ „ „ „  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O} + \text{D}_{1.2.2} + \text{D}_{1.1}$

„ *l*, „ „ „ „  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O} + \text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{D}_{1.1}$

As the equilibria represented in fig. 2 only apply to one definite temperature *T* and one definite pressure *P*, we have at 60° the following equilibria:

A. Invariant (*P. T*) equilibria.

1. binary: the point *a*, *c* and *e*.

2. ternary: „ „ *b*, *d*, *f*, *g* and *k*.

3. quaternary: „ „ *i*, *h* and *l*.

B. Monovariant (*P. T*) equilibria.

1. ternary: the curves *ab*, *bc*, *cd*, *de*, *ef*, *fg*, *gk* and *ka*.

2. quaternary: „ „ *bl*, *kl*, *lh*, *gh*, *hi*, *fi* and *id*

C. Divariant (*P. T*) equilibria.

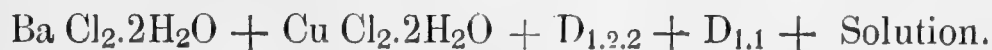
1. quaternary: the planes I, II, III, IV and V.

It is evident that between the Figs. 1 and 2 there exist transition forms, which must occur between 40° and 60°. If we start from fig. 2 and lower the temperature, the saturation surface *V* gets smaller until at 57° the points *g* and *k* coincide. The saturation surface then has a triangular form of which one apex rests against the side plane *W—CuCl<sub>2</sub>—KCl* of the tetrahedron. As in this apex the saturation surfaces I, IV, and V meet, the equilibrium:



occurs in the ternary system *KCl—CuCl<sub>2</sub>—Water* at 57°.

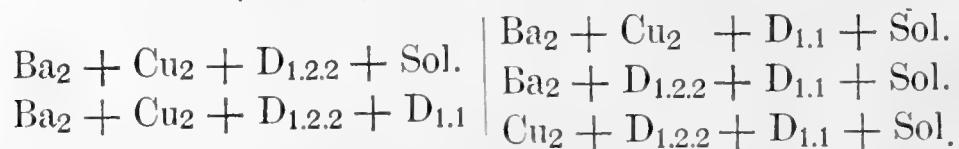
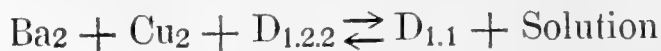
On lowering the temperature still further the saturation surface *V* becomes smaller still and surrounded by the saturation surfaces *I*, *III* and *IV* to finally disappear in a point within the tetrahedron, so that the relations drawn in fig. 1 occur. The moment the saturation surface *V* disappears, or rather that it becomes metastable, the surfaces *I*, *III*, *IV*, and *V* pass through *one* point so that only one single point of the surface *V* represents a stable solution. This then signifies that in the quaternary system occurs the invariant (*P*) equilibrium:



This as deduced from the thermic determinations, happens at ± 55.7°.

Between the above 5 phases a phase reaction may take place at 55.7°, on increase, or decrease of heat.

If, for the sake of brevity, we call  $\text{Ba Cl}_2 \cdot 2\text{H}_2\text{O} = \text{Ba}_2$  and  $\text{Cu Cl}_2 \cdot 2\text{H}_2\text{O} = \text{Cu}_2$ , the reaction is then:



Hence, of the invariant ( $P$ ) equilibrium two monovariant ( $P$ ) proceed to lower and three to higher temperatures, or if we only consider the systems in which a solution occurs, one to lower and three to higher temperatures.

The system proceeding to lower temperatures:  $\text{Ba}_2 + \text{Cu}_2 + \text{D}_{1.2.2} + \text{sol.}$  still exists at  $40^\circ$  and is represented in fig. 1 by the point  $h$ . The system proceeding to higher temperatures:  $\text{Cu}_2 + \text{D}_{1.2.2} + \text{D}_{1.1} + \text{solution}$  terminates at  $57^\circ$ , when the solution only still contains the three components  $\text{CuCl}_2$ ,  $\text{KCl}$  and water.

The other two systems proceeding to higher temperatures still exist at  $60^\circ$ ; the solution of the system  $\text{Ba}_2 + \text{Cu}_2 + \text{D}_{1.1} + \text{solution}$  is represented in fig. 2 by the point  $l$  and that of the system:  $\text{BaCl}_2 + \text{D}_{1.2.2} + \text{D}_{1.1}$  is indicated in fig. 2 by the point  $h$ .

**Chemistry.** — “*The system  $\text{HgCl}_2$ — $\text{CuCl}_2$ — $\text{H}_2\text{O}$ .*” By Prof. F. A. H. SCHREINEMAKERS and J. C. THONUS.

(Communicated in the meeting of September 28, 1912).

In order to ascertain whether or not the salts  $\text{HgCl}_2$  and  $\text{CuCl}_2$  form a double salt, the isotherm of  $35^\circ$  was determined; the result of this investigation is that, at  $35^\circ$  no double salt was found but that the salts  $\text{HgCl}_2$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  can exist by the side of each other.

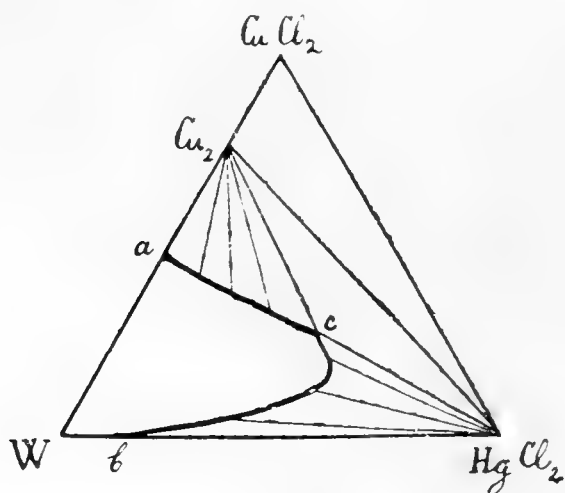


Fig. 1.

In fig. 1, the experimentally determined isotherm of  $35^\circ$  is represented schematically; the apexes  $W$ ,  $\text{HgCl}_2$  and  $\text{CuCl}_2$  represent the three components, and the point  $\text{Cu}_2$  the hydrate  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .

The isotherm consists of the two branches  $ac$  and  $bc$ ;  $ac$  indicates the solutions which are saturated with the hydrate  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $bc$  those saturated with



$\text{HgCl}_2$ ; the point of intersection  $c$  of the two saturation lines represents the solution saturated with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{HgCl}_2$ .

The solubility curve  $bc$  of the  $\text{HgCl}_2$  has a peculiar form; for a tangent may be drawn to it parallel to the side  $W \cdot \text{CuCl}_2$ . This means, in our case, that the solubility of  $\text{HgCl}_2$  first increases and then decreases with an increased  $\text{CuCl}_2$ -content of the solution. From the Fig. 1 it is shown that the solubility of  $\text{HgCl}_2$  is much increased by addition of  $\text{CuCl}_2$ ; from the table we see that the solubility of  $\text{HgCl}_2$ , which in pure water amounts to 8.51 % can increase to fully 52 % by addition of  $\text{CuCl}_2$ .

The isotherm represented schematically in fig. 1 can be drawn with the aid of the determinations communicated in the table. As not only the compositions of the liquids, but also those of the corresponding "residues" have been determined, the composition of the solid substance may be deduced therefrom. We find that the solutions of branch  $ac$  are saturated with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and those of  $bc$  with  $\text{HgCl}_2$ .

Compositions in % by weight at 35°.

of the solution		of the residue		solid phase
% $\text{CuCl}_2$	% $\text{HgCl}_2$	% $\text{CuCl}_2$	% $\text{HgCl}_2$	
44.47	0	—	—	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$
33.5	21.03	51.0	13.04	"
26.07	37.3	55.82	16.97	"
23.31	44.47	54.77	19.70	"
21.49	50.45	43.60	36.63	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{HgCl}_2$
21.47	50.60	15.08	74.35	" + "
21.54	50.37	—	—	" + "
19.40	52.44	3.0	91.94	$\text{HgCl}_2$
18.48	52.54	4.6	87.57	"
18.06	52.81	3.17	90.06	"
14.73	51.03	—	—	"
5.94	49.5	—	—	"
2.64	23.87	—	—	"
0	8.51	—	—	"

One of us has previously deduced the rule<sup>1)</sup> that the metastable continuations of the branches  $ac$  and  $bc$  must fall both together either within or without  $\angle Cu_2; c.HgCl_2$ . Which case occurs here is difficult to prove experimentally as both branches, in the vicinity of point  $c$  practically coincide with the sides of the angle  $Cu_2.c.HgCl_2$ . Moreover, the saturation line  $bc$  of the  $HgCl_2$  exhibits a very peculiar form. The metastable continuation must, of course, terminate somewhere on the side  $HgCl_2-CuCl_2$  of the triangle; from the course of the stable part in the vicinity of  $c$ , it appears, however, that this will not be possible without a point of inflexion appearing somewhere on the metastable part or on the stable part situated in the vicinity of  $c$ .

**Chemistry.** — “*The system Tin-Iodine*”. By Prof. W. REINDERS and S. DE LANGE. (Communicated by Prof. SCHREINEMAKERS.)

(Communicated in the meeting of September 28, 1912).

1. Of tin and iodine two compounds are known, stannous and stannic iodide. As regards the preparation and properties of these compounds there exist in the literature different conflicting statements. By the older investigators<sup>2)</sup>, for instance, it is stated that on heating tin with iodine, stannous iodide is formed. HENRY<sup>3)</sup>, however finds a mixture of  $SnI_2$  and  $SnI_4$  and PERSONNE<sup>4)</sup>  $SnI_4$  only. The melting point of  $SnI_4$  is given by PERSONNE<sup>5)</sup> as  $145^\circ$  (solidifying point  $142^\circ$ ), by EMICH<sup>6)</sup>  $143^\circ$ . The boiling point according to PERSONNE is at  $295^\circ$ , EMICH finds  $341^\circ$ . HENRY, however, states that it sublimes at  $180^\circ$ .

Of  $SnI_2$  the melting point is given both at  $246^\circ$ <sup>7)</sup> and at a dull red heat (PERSONNE) and the boiling point both at  $295^\circ$ <sup>7)</sup> and at the temperature of molten glass (PERSONNE).

For the knowledge of the binary systems of a metal and a metalloid a renewed investigation was therefore desirable.

2.  $SnI_4$  was prepared in two ways, *a.* by treating granulated tin for some days with a solution of iodine in carbon disulphide and

1) F. A. H. SCHREINEMAKERS, Die heter. Gleichg. von BAKHUIS ROOZEROM. III'. 268.

2) I. a. BERZELIUS, *Traité de chimie*; RAMMELSBERG, *Pogg. Ann.* **48**, 169.

3) *Phil. Trans.* **135**, 363 (1845).

4) *Compt. rendus.* **54**, 216 (1862).

5) *l. c.*

6) *Sitzungsber. der K. Ak. v. W. Wien* **113**, IIb, 535 (1904) (*Monatshefte* **25**, 907).

7) COHEN, *Abegg's Handbuch d. anorg. Ch.* III. 2, 571.

evaporating the solution obtained, *b.* by melting iodine with a small excess of tin. The weighed out quantities were introduced in small portions into a glass tube and if necessary, heated a little to start the reaction; the tube was then sealed, heated for some time at  $250^{\circ}$ ; then placed vertically and cooled slowly. The orange-red crystalline mass obtained was then separated from the tin and the bottom layer of crystals and reduced to a fine powder. Both methods gave according to analysis, pure  $\text{SnI}_4$  without any  $\text{SnI}_2$  whatever. Found: 18,95—18,99 % of Sn; theory 18,99 %.

For the preparation of  $\text{SnI}_2$  is recorded *a.* addition of  $\text{SnCl}_2$ -solution to KI-solution <sup>1)</sup> *b.* dissolution of tin in concentrated hydriodic acid <sup>2)</sup>.

The first method seems the most simple one. It has the disadvantage however, that in this reaction besides the red  $\text{SnI}_2$ , double salts with KI may be formed also, whilst it is still uncertain whether a protochloro-iodide (HENRY), or mixed crystals with  $\text{SnCl}_2$  are perhaps obtained in addition. The first method was, therefore, abandoned and the second process used instead. The action of tin on HI proceeds slowly and was carried out in a round bottomed flask attached to a refluxcondenser. The red crystals obtained were dried in a vacuum desiccator, first for a few weeks over sticks of KOH, then for a few months over  $\text{P}_2\text{O}_5$ . Found 31,83 and 31,87 % of Sn; theory 31,92 %.

Another mode of preparation will be mentioned presently.

3. The melting point of  $\text{SnI}_4$  was found  $143,^{\circ}5$ , therefore in agreement with EMICH, who gives  $143^{\circ}$ .

The solidifying point determinations of I- $\text{SnI}_4$ -mixtures took place in the usual manner by cooling in the apparatus VAN EIJK. In order to prevent strong undercooling we constantly stirred with the thermometer during the cooling.

The results are united in the subjoined table (p. 476) and represented graphically in Fig. 1.

Hence we have a simple melting point line with a eutecticum at  $79,^{\circ}6$  and 60 % by weight of  $\text{SnI}_4$  (12,06 at. % Sn).

4. In the preparation of  $\text{SnI}_4$ , it had already been shown that  $\text{SnI}_4$  could be heated for a considerable time with Sn at  $250^{\circ}$  without any perceptible reaction setting in with formation of  $\text{SnI}_2$ .

The possibility had, therefore, to be considered whether Sn and

<sup>1)</sup> BOULLAY, Ann. d. phys. et chim. (2) **34**, 337 (1827); PERSONNE, l. c.

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

Composition of the liquid		Initial Solidifying point
gr. SnI <sub>4</sub> per 100 gr. SnI <sub>4</sub> + I	at. Sn per 100 at. Sn + I	
0	0	113.2
10	2.02	109.0
20	4.04	104.7
30	6.05	99.7
40	8.06	94.7
50	10.06	87.6
55	11.06	83.0
60	12.06	79.6
65	13.05	83.5 (eutecticum 79°6)
70	14.05	89.8
80	16.04	108.4
90	18.02	127.0
100	20.00	143.5

SnI<sub>4</sub> might not really be in stable equilibrium with each other and that SnI<sub>2</sub> might be at high temperature a labile compound that would dissociate into Sn + SnI<sub>4</sub>. Looking at the fact that the number of halogen atoms, capable of combining with an element, generally decreases with the atomic weight of the halogen, the probability of this was not great, and it was even to be expected that SnI<sub>2</sub> would be very permanent.

In order to decide this, weighed quantities of Sn, SnI<sub>4</sub>, and SnI<sub>2</sub> were heated in a sealed tube during 14 hours at 360°. Starting from 12.5 grams of SnI<sub>4</sub>, 7.7 grams of SnI<sub>2</sub> and 2.4 grams of Sn there were obtained about 9.6 grams of SnI<sub>4</sub>, 10.5 grams of SnI<sub>2</sub> and 1.6 gram of Sn. Consequently, there was a very appreciable decrease of Sn and SnI<sub>4</sub> and an increase of SnI<sub>2</sub>.

The reaction  $\text{Sn} + \text{SnI}_4 \rightarrow 2 \text{SnI}_2$ , therefore, actually does take place, although very slowly. The contradiction between the statement of PERSONNE that from Sn + I no SnI<sub>2</sub> is formed and that of HENRY, who states that a mixture of SnI<sub>4</sub> and SnI<sub>2</sub> is formed, is now explained. HENRY has evaporated SnI<sub>4</sub> with an excess of fine tin powder and so obtained a partial conversion into SnI<sub>2</sub> which was

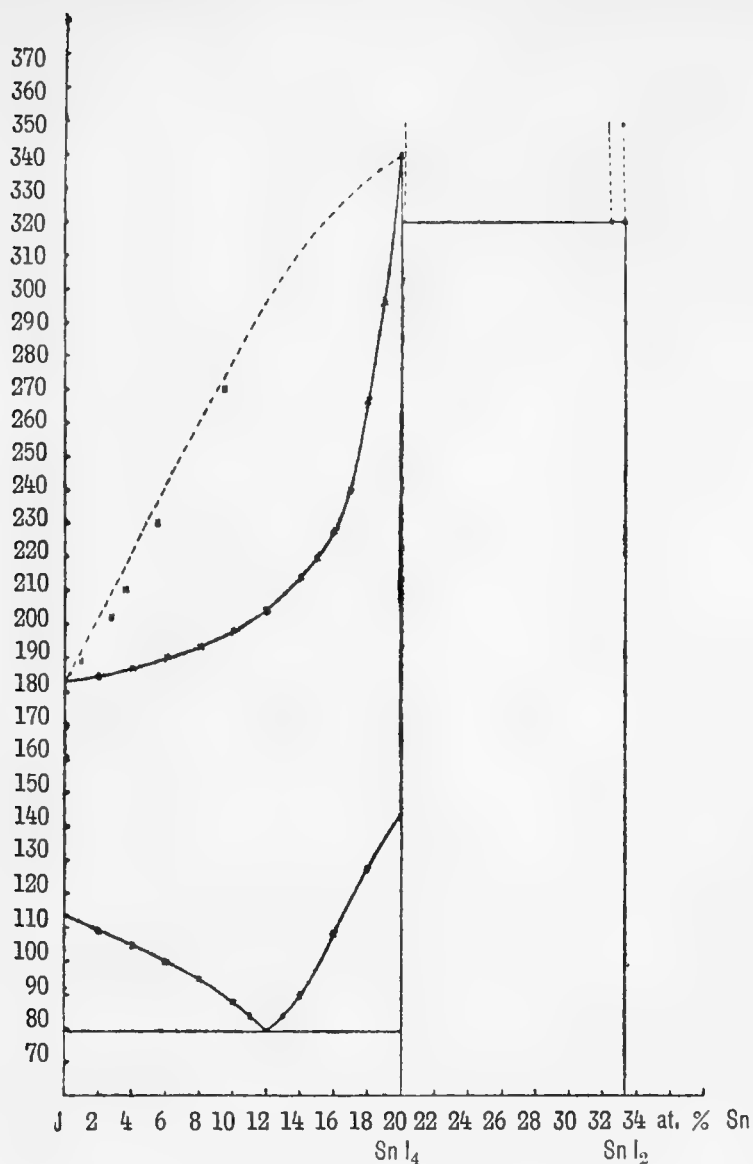


Fig. 1.

left on evaporation. PERSONNE allowed but a short time for the reaction and took no particular care to accelerate the same by addition of an excess of fine tin powder, and so he got no appreciable quantities of Sn I<sub>2</sub>.

By this conversion is now indicated also another method for the preparation of Sn I<sub>2</sub>, namely, prolonged heating of Sn + Sn I<sub>4</sub> in a sealed tube at a high temperature (360°).

It appears that Sn I<sub>2</sub> and Sn I<sub>4</sub> then form two liquid layers, a bottom layer of Sn I<sub>2</sub> and an upper layer of Sn I<sub>4</sub>. In order to promote the reaction it is, therefore, necessary to keep on shaking the tube so as to bring the Sn I<sub>4</sub> into contact with the Sn. By placing the tube, at the end of the heating operation, in a vertical position, and then allowing it to cool, we obtain, after solidification a crystalline stick which can be readily removed from the tube and breaks up along a fairly sharp meniscus into a SnI<sub>2</sub> and a SnI<sub>4</sub> piece. By strongly heating in a test tube of hard glass, the Sn I<sub>2</sub> can be freed from the adhering SnI<sub>4</sub>.

The analysis of the  $\text{Sn I}_2$ , thus prepared gave 31.6 and 31.2 % of tin instead of the theoretical quantity (31.9).

5. The melting point of  $\text{Sn I}_2$  was determined by heating and cooling in a small electric furnace consisting of a cylindric little pot of porous earthenware, surrounded by a nickel heating wire and placed in a similar larger pot which was then filled up with asbestos. The melting point was found at  $319^\circ\text{--}320^\circ$ .

The boiling point of  $\text{Sn I}_2$  was determined in a 25 cm. long hard glass tube 3—4 cm. in diameter, the upper part of which was thoroughly isolated by a thick layer of asbestos and could be heated electrically by a nickel wire, whilst the lower part, which contained the  $\text{Sn I}_2$ , was heated strongly either electrically or with the blow-pipe. The temperature was measured with a standard Pt-PtRh thermocouple.

The mean of many determinations was  $720^\circ$ .

6. Addition of  $\text{Sn I}_4$  or Sn had no perceptible influence on the melting point of  $\text{Sn I}_2$ . These substances, when by the side of  $\text{Sn I}_4$ , form a second liquid phase, so that above  $320^\circ$  there are two regions of decomposition, one between  $\text{Sn I}_4$  and  $\text{Sn I}_2$  and one between  $\text{Sn I}_2$  and Sn. The fused  $\text{Sn I}_2$  lies in a narrow region of homogeneous mixing.

In order to determine the limits of these regions of decomposition,  $\text{Sn I}_2$  and  $\text{Sn I}_4$  were heated in a narrow sealed tube and shaken for an hour at  $350^\circ$  in an electric tube furnace. The apparatus was then placed in a vertical position, the tube was removed and rapidly cooled in a current of air. The solidified  $\text{Sn I}_2$  and  $\text{Sn I}_4$  layers were separated from each other, well scraped and then analysed.

*The  $\text{Sn I}_4$  layer.* The total tin content was 18.95 and 19.02, mean 18.99, which corresponds to pure  $\text{Sn I}_4$ . The solubility of  $\text{Sn I}_2$  in  $\text{Sn I}_4$  is therefore, practically *nil*. This result was confirmed by dissolving a portion of the upper layer in carbon disulphide and after adding iodine, titrating the excess of the latter with sodium thiosulphate; only 0.06 % of  $\text{Sn I}_2$  was thus found.

*The  $\text{Sn I}_2$  layer.* The total tin content amounted to 31.2 and 30.9 %, mean 31.1 %;  $\text{Sn I}_2$  requires 31.9 % of tin. This analysis therefore points to a 6 %  $\text{Sn I}_2$  content. This figure must probably be considered as a maximum. During the fusion the  $\text{Sn I}_4$  penetrates between the glass and the  $\text{Sn I}_2$  layer so that after cooling, this is enveloped by a thin layer of  $\text{Sn I}_4$  which might be not completely removed in some places. The fact that addition of  $\text{Sn I}_4$  does not

perceptibly affect the melting point of  $\text{SnI}_2$ , shows that the solubility of  $\text{SnI}_4$  in this layer is very trifling.

*The  $\text{SnI}_2$  layer saturated with Sn.*  $\text{SnI}_2$ , prepared by shaking molten  $\text{SnI}_4$  with Sn, did not differ in colour from that which had been prepared by the net process and fused afterwards. A solubility of Sn in  $\text{SnI}_2$  did not make itself conspicuous by a darker colour, or as LORENZ<sup>1)</sup> describes it by a "Metallnebel". The analysis of fused  $\text{SnI}_2$  which had been heated with Sn for some time at  $350^\circ$ — $400^\circ$  and then poured off from the molten metal, also did not differ perceptibly from that of pure  $\text{SnI}_2$ . The solubility of Sn in  $\text{SnI}_2$  is, therefore, exceedingly small. This is in agreement with the determinations of the solubility of Sn in  $\text{SnI}_2$  by R. LORENZ<sup>2)</sup>, who found that at  $629^\circ$  this is only 0.13 % more than at  $400^\circ$ , so that, at  $350^\circ$ , it may be safely taken as practically *nil*.

7. The boiling point of  $\text{SnI}_4$  was determined at  $340^\circ$ ; EMICH has stated it to be at  $341^\circ$ . These determinations therefore tally, and the previous statement by PERSONNE ( $295^\circ$ ) must be rejected as being inaccurate.

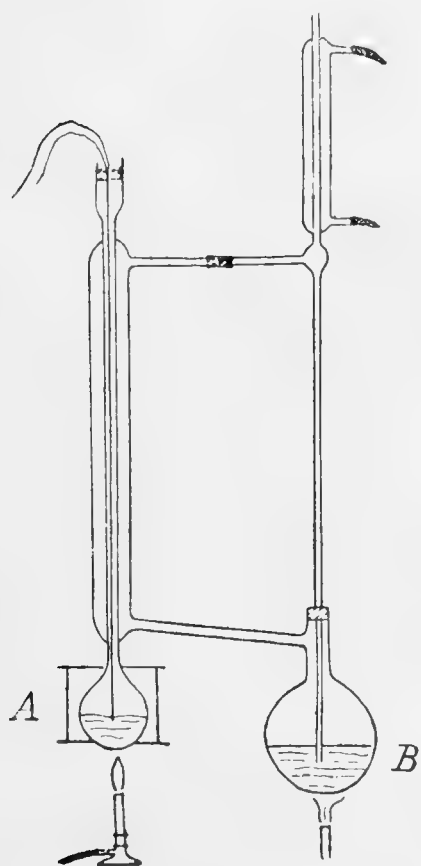


Fig. 2.

8. The boiling points of mixtures of I and  $\text{SnI}_4$  were determined in the apparatus drawn in Fig. 2. This consisted of a round-bottomed flask *A* of  $\pm 100$  cc capacity, half way filled with the boiling mixture and protected by an asbestos case in the bottom of which a circular opening was made. The boiling flask can then be heated over the naked flame without danger of superheating.

To the flask was sealed a vertical tube surrounded by a jacket which was heated up to  $140^\circ$  by xylene vapour from *B*. This prevented the vapour from *A* from forming a solid deposit in the tube; it condensed to liquid and was collected again in *A*.

If, after long boiling, the iodine vapour had diffused too much towards the upper part of the apparatus, the heating of *A* was suspended and all the iodine reentered the flask. The apparatus

1) R. LORENZ. Die Elektrolyse geschmolzener Salze.

2) R. LORENZ. Die Elektrolyse geschmolzener Salze II, 77.

gave great satisfaction. Not a trace of vapour was lost and by adding every time weighed quantities of  $\text{SnI}_4$  or I and starting from the pure components or of a mixture of known composition, a whole series of determinations could be carried out.

The temperature was recorded by means of a previously standardised thermo-couple of silver-constantan which was plunged into the boiling liquid.

The results are united in the following table.

Composition of the liquid.		Boiling point.
gr. $\text{SnI}_4$ per 100 gr. $\text{SnI}_4 + \text{I}$	at. Sn per 100 at. $\text{Sn} + \text{I}$	
0	0	183
10	2.02	184
20	4.04	187
30	6.05	190
40	8.06	193
50	10.06	198
60	12.06	204
70	14.05	214
75	15.05	219.5
80	16.04	228
85	17.03	240
90	18.02	267
95	19.01	296
100	20.00	340

9. Finally, we endeavoured to determine the composition of the saturated vapour which coexists with the different  $\text{SnI}_4 - \text{I}$  mixtures.

For this purpose the liquid was heated to boiling in a 25 c.m. long circular tube surrounded at its upper end by a thick asbestos jacket. In the vapour space was then placed a long suction tube with a pipette-like enlargement of 1—2 c.c., capillary drawn out and bent upwards at the lower end. By means of this tube some vapour close above the surface of the boiling liquid was withdrawn; this condensed for the greater part in the pipette and was then



analysed. Although these determinations have only a qualitative value, we still think it worth while to communicate the result.

Boiling point	Composition of the liquid.		Composition of the vapour.	
	in % SnI <sub>4</sub> by weight	in at. % Sn	in % SnI <sub>4</sub> by weight	in at. % Sn
185	13	2.6	2	0.4
189	27	5.4	5	1.0
201	55	11.0	14	2.8
210	66.5	13.3	18	3.6
230	81	16.2	28	5.6
270	91	18.2	48	9.6

*Summary of results.*

1. The melting point of SnI<sub>4</sub> is 143,°5, the boiling point 340°. The melting point of SnI<sub>2</sub> is 320°, the boiling point 720°.

2. In the action of Sn on I, there is at first an exclusive formation of SnI<sub>4</sub>. The reaction  $\text{SnI}_4 + \text{Sn} = 2 \text{SnI}_2$  takes place with extreme tardiness and even at 350° it still proceeds at a very slow rate.

3. The melting point line of mixtures of SnI<sub>4</sub> and I consists of two branches with a eutecticum at 79°,6 and 60 % by weight of SnI<sub>4</sub> (12,06 at. % Sn). The boiling point line takes a regular course without a maximum or a minimum.

4. Fused SnI<sub>2</sub> and SnI<sub>4</sub> form two liquid layers, the composition of which at 350° is: SnI<sub>4</sub> with traces only of SnI<sub>2</sub> and SnI<sub>2</sub> with at most 6 % of SnI<sub>4</sub>. As Sn also is not perceptibly soluble in molten SnI<sub>2</sub>, this lies in a very narrow region of homogeneous mixing which, at 350°, extends from 33,3 at. % Sn (pure SnI<sub>2</sub>) to 32,5 at. % Sn (SnI<sub>2</sub> + 6 % by weight of SnI<sub>4</sub>).

*Inorg. Chem. Laboratory  
Technical High School.*

*Delft, June 1912.*

**Chemistry.** — “*The distribution of dyestuffs between two solvents. Contribution to the theory of dyeing.*” By Prof. W. REINDERS and D. LELY Jr. (Communicated by Prof. F. A. H. SCHREINEMAKERS.)

(Communicated in the meeting of September 28, 1912).

For the explanation of the absorption and retention of dyestuffs by fibres there exist three theories; the chemical theory, the theory of solid solution, and the mechanical or adsorption theory.

According to the first theory <sup>1)</sup> the colouring matter enters into a chemical reaction with a constituent of the fibre with formation of an insoluble product, which is retained in the fibre. This constituent — according to KNECHT, lanolinic acid in wool and sericinic acid in silk — is supposed to have the character of an amphoteric electrolyte and, therefore, to be capable of forming a salt with the base of the basic dyestuffs as well as with the acid of the acid dyestuffs.

An important argument in favour of this theory is the observation that when dyeing with basic dyestuffs there first occurs a dissociation into base and acid, the former then being absorbed by the fibre and the latter retained in the bath.

But it appears, however, that this dissociation also takes place in the absorption of dyestuffs by cotton, by pure cellulose <sup>2)</sup> and by inorganic matters such as glass, asbestos, silicates <sup>3)</sup>, and carbon <sup>4)</sup> in which substances we surely cannot assume the presence of an acid capable of forming a salt with the dissociated base.

Moreover, the occurrence of such a dissociation in the case of acid dyestuffs is still doubtful <sup>5)</sup>, and it also does not take place with the substantive colouring matters which are absorbed in their entirety. The chemical method of explanation is here a complete failure.

We also might be led to expect that the amount of colouring matter that can be absorbed by a certain fibre would be determined by the quantity of acid or base in that fibre. Only so much colouring matter ought to be taken up as is equivalent to this content in acid or base and a further addition of colouring matter to the bath should not cause any further absorption of the dyestuff by the fibre. More-

<sup>1)</sup> KNECHT, Berl. Ber. **21**, 1556, 2804; **22**, 1120 (1889). SUIDA, Sitzungsber. der K. Akad. d. Wiss. Wien. **113** II<sub>B</sub>, 725 (1904); Z. f. angew. Chem. 1909, 2131.

<sup>2)</sup> KNECHT, Färberzeitung **18**, 22 (1893/94).

<sup>3)</sup> GEORGIEVICS, Färberzeitung **19**, 9, 129, 188, 286 (1894/95).

<sup>4)</sup> FREUNDLICH und LOSEV. Z. f. physik. Chem. **59**, 284 (1907); Losev, Inaug. Dissert. Leipzig 1907, p. 45.

<sup>5)</sup> LOSEV, l. c. p. 67.

over, the formation of the insoluble precipitate in the fibre could only start when a certain concentration had been attained in the bath.

Neither of these phenomena have, however, been observed. The absorption of the dyestuff increases regularly with its concentration in the bath and there is no question of a discontinuity in this absorption.

The chemical theory is, therefore, an improbable one and is, in fact, rejected by the majority of the investigators of dye absorptions.

The theory of the solid solution has been proposed first by O. N. WITT<sup>1)</sup> and was at first universally accepted. WITT, by a number of examples has rendered it indeed plausible that the condition in which the colouring matter is present in the fibre is perfectly comparable with that of a substance in solution, that there is an equilibrium between the dyestuff in the fibre and in the aqueous solution and that the changes in that equilibrium, caused by the addition of another solvent such as alcohol, or of acids or salts, agree qualitatively, exactly with those in the equilibrium between two non-miscible liquids in which a third substance is dissolved.

In the quantitative investigation as to the distribution of the dyestuff between the fibre and the bath, it has been found, however, that this distribution does not take place according to

HENRY'S law, but that the adsorption-formula  $\frac{x}{m} = ac^{1/n}$  must be applied.

Mainly on account of this, WALKER and APPLEYARD<sup>2)</sup> as well as SCHMIDT<sup>3)</sup>, FREUNDLICH and LOSEV<sup>4)</sup>, GEORGIEVICS<sup>5)</sup>, PELET-JOLIVET<sup>6)</sup> and others conclude that WITT'S theory cannot be correct and that the colouration is, in the first instance, an adsorption phenomenon<sup>7)</sup>.

Hence, a very high value is attached to this utterly empirical and very elastic formula, which in FREUNDLICH and LOSEV'S determinations

<sup>1)</sup> Färberzeitung 1890/91, 1.

<sup>2)</sup> Journ. Chem. Soc. **69**, 1334 (1896).

<sup>3)</sup> Zeitschr. f. physik. Chem. **15**, 56 (1894).

<sup>4)</sup> l.c. and FREUNDLICH, Koll. Zeitschr. **3**, 212 (1908).

<sup>5)</sup> l.c.

<sup>6)</sup> L. PELET-JOLIVET, Die Theorie des Färbeprozesses, 1910.

<sup>7)</sup> According to FREUNDLICH and LOSEV the fixation of the dye after its absorption, takes place because the colouring matter was either dissolved in a colloidal state and then rendered insoluble by coagulation by the fibre (in the case of substantive dyes), or was dissolved molecularly but converted in the fibre into an insoluble or colloidal non-diffusing substance. As regards this last change the action of another adsorbed substance (the mordant) or of the fibrous matter would, however, have to be considered eventually.

PELET-JOLIVET also regards the fixation of the dye chiefly as a coagulation of colloids.

had actually to be modified so as to agree with the figures obtained.

The question now arises whether this is really justified.

Is the compliance with this formula really such a certain criterion for the presence of a surface condensation, or can we meet with a similar relation in the distribution of a dyestuff over two non-miscible liquids?

Again, are the other properties of the dyed fibre in harmony with the adsorption theory? Is the colouring matter really present at the surface only or must we assume that it has penetrated also in the interior of the same?

We will consider these questions successively.

How is the dyestuff distributed in the fibre?

Some years ago this question was fully discussed by HUGO FISCHER<sup>1)</sup>, who has most strongly protested against the implicit belief in internal surfaces in colloids. He calls attention to the fact that with starch granules, for instance, the colouration is perfectly homogeneous and argues in detail and on several grounds that the assumption that we are dealing with an adsorption is very improbable. He points out that the appearance of the coloured granule as well as the progressive change of the colouring process with a slowly acting dye stuff such as congo-red makes altogether the impression that this colouration is a phenomenon of solution and not a surface condensation. SUIDA<sup>2)</sup> in his investigations on the dye absorption of starch granules, also states that they are coloured quite homogeneously. The fact that when a dyestuff in the solid condition has a colour different to that of its solution, the fibre always presents the colour of the latter and not that of the former<sup>3)</sup> also shows that the dyestuff is present in a condition which corresponds with solution.

In the case of several other phenomena which have been described as adsorptions, a doubt now begins to arise whether this view is really quite correct. VAN BEMMELEN<sup>4)</sup> has already pointed out that with the gels the line between *ad-* and *absorption* is difficult to draw. DAVIS<sup>5)</sup> found that the amount of iodine taken up by carbon increases with the time of action. The iodine diffuses slowly towards the interior of the carbon. MC BAIN<sup>6)</sup> noticed the same in the absorption

1) Z. f. physik. Chem. **63**, 480 (1908).

2) Sitzungsber. der K. Akad. d. Wiss. Wien **113** II B, 725 (1904).

3) O. N. WITT, l.c.

4) Z. f. Anorg. Chem. **23**, 321 (1900).

5) Journ. Chem. Soc. **91**, 1666 (1907).

6) Z. f. physik. Chem. **68**, 471 (1909).

of hydrogen by carbon and concludes that a portion is really adsorbed and that another portion forms a solid solution.

GEORGIEVICS<sup>1)</sup>, in his later investigations as to the absorption of dilute acids by wool, has also come to the conclusion that in many cases adsorption and solid solution occur together. From very dilute solutions, acids as well as different colouring matters with a constant division factor are absorbed so that this absorption may be considered as a true solid solution.

Adsorption and solution, therefore, go hand in hand and in most cases it is difficult to make out what part appertains to each of these phenomena.

When the nature of the absorbing material causes the diffusion towards the interior to take place with extreme difficulty, as in the case of carbon and silicates, the formation of a solution will take place in the external layers of the substance only and one will get the impression of dealing with a mere surface action or adsorption. In some cases, however, it appears that the colouring matter has penetrated further into the substance. Silicates coloured by fuchsine and methylene blue exhibit a distinct pleochroism<sup>2)</sup>, which shows that the dyestuff has distributed itself homogeneously *into* the silicate and has not deposited merely on the surface.

Cases of true adsorption will occur when the substance is dissolved in the colloidal state and does not dissolve molecularly in the absorption medium. We may then expect either no absorption at all or a complete absorption as colloidal solid solution, or else a complete separation of the colloid at the border layer; this then constitutes adsorption. Instances of this are found in the adsorption of colloidal gold by carbon or by BaSO<sub>4</sub><sup>3)</sup>, of As<sub>2</sub>S<sub>3</sub>-solution by carbon or by BaSO<sub>4</sub>, of a very fine carbon suspension by paper<sup>4)</sup> and also in the dyeing of wool or cotton with some undoubtedly colloidal dye solutions such as that of the blue acid of congo-red. This colouration however, is not permanent and can be completely removed by washing<sup>5)</sup>.

How does a dyestuff distribute itself over two solvents?

In this direction but few determinations have been made. Only in the case of picric acid the distribution between water and

<sup>1)</sup> Koll. Zeitschr. **10**, 31 (1912),

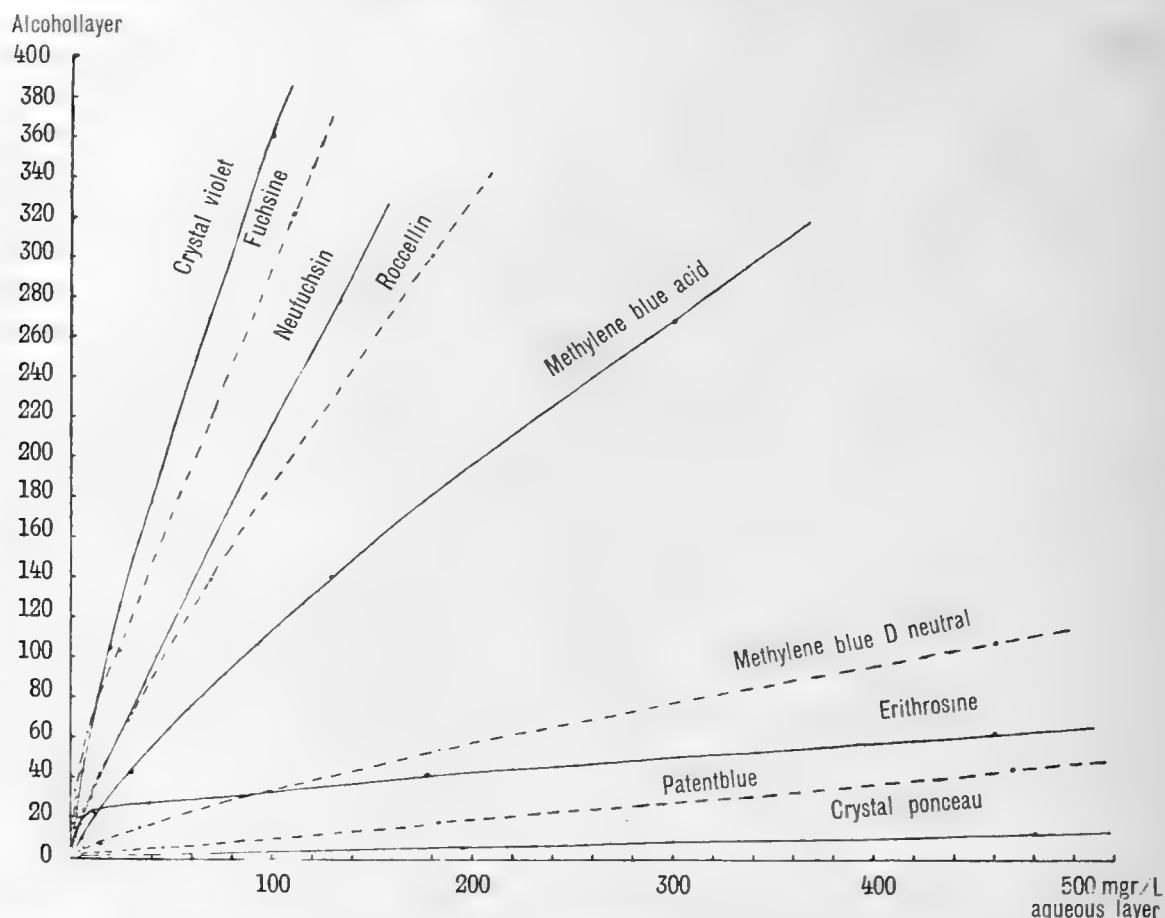
<sup>2)</sup> T. CORNU, Tschermak's Mineralogische und Petrographische Mitteilungen 1906, 453.

<sup>3)</sup> L. VANINO, Berl. Ber. **35**, 662 (1902).

<sup>4)</sup> SPRING, Beobachtungen über die Waschwirkung der Seifen. Koll. Zeitschr. **4**, 161 (1909).

<sup>5)</sup> PELET-JOLIVET, Die Theorie des Färbeprozesses, p. 141

various organic solvents such as amyl alcohol, benzene, chloroform, bromoform and toluene has been investigated and it has been found



that on increasing the concentration an proportionally smaller part remains in the aqueous layer<sup>1)</sup>. With methylene blue, between aniline and water, the division coefficient is constant<sup>2)</sup>.

We have now measured for a number of dyestuffs the distribution between water and isobutyl alcohol (b.p. 106°). The determination of the colouring matter was effected colorimetrically. The temperature was 25°. The results are united in tables 1—19. The concentrations are indicated therein in mgs. per litre.

From these tables and better still from the curves in fig. 1 it appears that with all these colouring matters, the division coefficient  $\frac{c_a}{c_w}$  decreases with the increase in the concentration. If the adsorption

relation  $c_a = a \frac{1}{w^n}$  is applied we find that  $\frac{1}{n}$  varies from 0.3 (with erythrosine A) to 1 (alkali blue and crystal ponceau). In most cases, however, this exponent increases with the rise of the concentration.

This result is surprising. As the investigations of recent years have

<sup>1)</sup> W. HERZ, Der Verteilungssatz, Sammlung chem. und chem.-techn. Vorträge 15 (1909).

<sup>2)</sup> PELET-JOLIVET, Revue gén. mat. col. 1909, 249.

1. *Methyleneblue* G. conc. (Basel).  
(Basic dyestuff).

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
1.6	4.3	2.70	0.20	0.633	0.56
5.8	8.7	1.50	0.76	0.939	
15.4	15	0.97	1.19	1.176	
37	24	0.65	1.57	1.38	
78	50	0.64	1.89	1.70	
140	72	0.51	2.14	1.85	0.72
464	156	0.34	2.66	2.19	

2. *Methyleneblue* G. conc.  
Aqueous layer 0.33 n. HCl.

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
0.32	2.27	7.09	0.505-1	0.356	0.75
3.2	9.0	2.75	0.505	0.954	
11.6	22.5	1.95	1.064	1.352	"
29.6	43.0	1.45	1.471	1.642	"
130	140	1.08	2.114	2.146	"
304	268	0.88	2.483	2.428	"

3. *Methyleneblue* G. conc.  
Aqueous layer 0.003 n. KOH.

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
4.0	18.0	4.50	0.602	1.255	0.75
9.0	32.5	3.61	0.954	1.512	
25	70	2.80	1.398	1.875	"
120	200	1.67	2.079	2.301	"
300	500	1.67	2.477	2.699	"

4. *Methyleneblue* D (Basel).  
Neutral.

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
6.8	5.2	0.76	0.832	0.716	0.72
15.0	6.9	0.46	1.176	0.839	
34	15.5	0.45	1.531	1.190	"
184	54	0.30	2.265	1.732	"
460	108	0.24	2.663	2.033	"

5. *Methyleneblue* D.  
With 2 equivalents of HCl.

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
7	7.5	1.07	0.845	0.875	0.65
15	10.5	0.70	1.176	1.021	
38	22.4	0.60	1.580	1.350	0.84
165	79	0.48	2.217	1.898	
440	192	0.44	2.643	2.283	

6. *Fuchsine*.  
(Basic dyestuff).

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
0.75	18	24.0	0.87-1	1.25	0.4
2.5	35	14.0	0.40	1.54	
8.0	62	7.75	0.90	1.79	0.7
24	103	4.30	1.38	2.01	
110	320	2.91	2.04	2.50	
320	620	1.94	2.50	2.79	"

7. *Fuchsine*.  
With 7 equivalents of HCl.

$C_w$	$Ca$	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
5.3	42	8.0	0.724	1.623	1.0
14	118	8.4	1.146	2.072	
25	232	9.3	1.398	2.365	
52	450	8.65	1.716	2.653	
140	1108	7.91	2.246	3.045	

8. *Crystal violet* (Basel).  
(Basic dyestuff).

$C_w$	$Ca$	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
0.9	17	18.9	0.95-1	1.23	0.5
2.0	25	12.5	0.30	1.40	
5.3	43.5	8.2	0.72	1.64	
19.5	104	5.3	1.29	2.02	
100	360	3.6	2.00	2.56	0.9
245	820	3.35	2.40	2.91	

9. *Neufuchsin* (Höchst).  
(Basic dyestuff).

$C_w$	$Ca$	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
2.0	12.5	6.5	0.30	1.10	0.5
4.0	17.5	4.4	0.60	1.24	
9.4	30	3.2	0.97	1.48	
28	68	2.4	1.45	1.83	
120	250	2.1	2.08	2.40	
290	600	2.1	2.46	2.78	1.0
780	1560	2.0	2.89	3.19	
1600	3000	1.9	3.20	3.48	
3200	5700	1.8	3.50	3.76	

10. *Crystal ponceau*.  
(Acid dyestuff).

$C_w$	$Ca$	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
20	1	0.05	1.301	0.00	1.0
49	1.7	0.035	1.690	0.230	
195	6.0	0.031	2.290	0.778	"
480	15.0	0.031	2.681	1.176	"

11. *Patent blue* (Höchst).  
(Acid dyestuff).

$C_w$	$Ca$	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
4.2	1.0	0.24	0.62	0.00	0.6
8.5	2.1	0.25	0.93	0.32	
46	5.4	0.12	1.66	0.73	
184	18.0	0.098	2.26	1.25	
470	45.4	0.095	2.67	1.66	
1140	150	0.13	3.06	2.18	1.25
2250	375	0.17	3.35	2.57	

12. *Erithrosine A*. (Höchst).  
(Acid dyestuff).

$C_w$	$Ca$	$\frac{Ca}{C_w}$	$\log C_w$	$\log Ca$	$\frac{1}{n}$
1.4	11.0	7.9	0.146	1.041	0.30
4.0	16.8	4.2	0.602	1.225	
10.7	23.4	2.2	1.029	1.369	
38.5	27.7	0.72	1.587	1.442	
178	42	0.24	2.250	1.623	
460	63	0.14	2.663	1.799	"



13. *Roccellin* (Basel).  
(Acid dye stuff).

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
1.62	11.77	7.27	0.210	1.061	0.52
4.38	19.5	4.45	0.641	1.290	
14.2	42.6	3.0	1.152	1.629	
30.4	73.6	2.4	1.483	1.867	
65	138	2.1	1.813	2.140	0.80
179	300	1.7	2.253	2.477	

14. *Quinoline yellow* (Fr. Bayer).  
(Acid dyestuff).

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
11.5	18	1.60	1.06	1.25	1.0
23	38	1.64	1.36	1.58	
60	100	1.67	1.77	2.00	"
120	200	1.67	2.08	2.30	"
240	425	1.77	2.38	2.63	"
630	964	1.53	2.79	2.98	"

15. *Quinoline yellow*.  
With 10 equivalents of HCl.

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
6.5	36	5.5	0.81	1.56	1.0
12.5	74	6.0	1.10	1.87	
31	200	6.45	1.49	2.30	"
61	390	6.40	1.78	2.59	"
125	800	6.40	2.10	2.90	"
320	2030	6.39	2.51	3.31	"

16. *Quinoline yellow*.  
With 10 equivalents of KOH.

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
12	17	1.40	1.08	1.23	1.0
25	33	1.32	1.40	1.52	
70	80	1.14	1.84	1.90	"
140	160	1.14	2.15	2.20	"
280	320	1.14	2.45	2.51	"
720	800	1.11	2.86	2.90	"

17. *Alkali blue 6 B.* (Bayer).  
(Acid dyestuff).

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
7.9	105	13.3	0.897	2.021	1.0
15.1	212	14.0	1.179	2.326	
30.2	425	14.1	1.480	2.628	"

18. *Congo-red* (Bayer).  
(Substantive dyestuff).

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
9.0	2.2	0.24	0.954	0.342	0.77
19	3.3	0.17	1.279	0.518	
48	6.5	0.13	1.681	0.813	"
94	12	0.13	1.973	1.079	"
180	21	0.12	2.255	1.322	"
480	42	0.09	2.681	1.623	"

19. *Congo-red*.  
With 4 equivalents of KOH.

$C_w$	$C_a$	$\frac{C_a}{C_w}$	$\log C_w$	$\log C_a$	$\frac{1}{n}$
6.6	2.4	0.36	0.819	0.380	0.73
17.4	5.4	0.31	1.240	0.732	
44	10	0.23	1.643	1.000	"
180	27	0.15	2.255	1.431	"
456	60	0.13	2.654	1.778	"

shown that different dyestuffs, particularly the basic and the acid ones, are dissolved molecularly in aqueous solution and, as shown by the conductivity of those solutions, are fairly strongly dissociated electrolytically, whereas the dissociation in alcoholic solution is but trifling, we might expect that the transition into the alcohol layer would increase with a rise of the concentration.

In order to explain this small exponent we can make different suggestions:

1. The molecular size of the colouring matter is greater in the aqueous solution than in the alcoholic one.

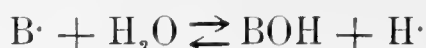
This view finds support in the determinations of KRAFFT<sup>1)</sup> on the lowering of the freezing point in aqueous and alcoholic solution. From these the following molecular weights are deduced:

	in water	in alcohol	theoretical
Fuchsine	520—617	320—344	337
Methyl violet	804—870	403—421	408
Benzopurpurin	3000	—	724
Diamine blue	3430	—	999

Hence, the two first basic dyestuffs would possess in water twice as great a molecular weight as in alcohol. These determinations, however, are not in harmony with the measurements of the conductivity power of most of the dyestuffs, dissolved as salts, which is about equal to that of a strongly dissociated binary electrolyte.

2. The dyestuff (BS) in aqueous solution is partly dissociated hydrolytically. By the alcohol the neutral molecules are strongly absorbed, the ions are not. In the case of a basic dyestuff the mols. BOH and BS therefore pass into the alcohol layer.

The hydrolysis equilibrium can be written as



hence

$$c_{BOH} \times c_{H} = k_1 c_B.$$

or also, because

$$c_{BOH} = c_H$$

$$c_{BOH} = \sqrt{k_1 c_B^{1/2}}$$

To the ordinary electrolytic dissociation of the dye salt applies the formula:

$$c_{BZ} = k_2 c_B \times c_{Z'} = k_2 c_B^2$$

<sup>1)</sup> Berl. Ber. 32. 1608 (1899).

If for the dye salt in the aqueous solution, we take it for granted that there is practically a complete dissociation, the concentration of the dye in the aqueous layer  $C_w$  may be considered as equal to  $c_B$ . If now we call the division coefficients for the molecules BOH and BS  $k_3$  and  $k_4$  we obtain:

$$\underline{C_a} = k_3 c_{\text{BOH}} + k_4 c_{\text{BZ}} = \underline{K_1 C_w^{1/2} + K_2 C_w^2}.$$

The first term will be of influence particularly with small concentrations; the second will apply more in the case of increased concentrations.

On applying the adsorption formula,  $\frac{1}{n}$  will, therefore, increase with the rise of the concentration. It will start with a value  $< 1$  then become  $= 1$  and may subsequently rise to above 1. The line indicating the dependence of the concentration in the alcohol layer on that in the aqueous layer will at first turn its concave side downwards, then exhibit a point of inflexion and finally turn its concave side in an upward direction.

A similar variation of  $\frac{1}{n}$  has indeed been observed with a great many dyestuffs even though with most of them no higher values than 1 were obtained. Only with "patent blue" this value was exceeded and  $\frac{1}{n}$  rose to 1.3.

In agreement therewith it also appears that in the case of basic dyestuffs, the transition into the alcohol layer is promoted by addition of a base and in the case of acid dyestuffs by addition of an acid and in such a manner that finally everything passes into the alcohol layer (see Table 20).

Reversely, however, by adding acid to a basic dyestuff, or a base to an acid dyestuff, the transition thereof into the alcohol layer is not diminished. Frequently, this even causes an increase in the concentration of the alcohol layer.

This may be partly explained by the diminution in the hydrolysis, and the increase in the concentration of the non-dissociated salts caused thereby. From the changes in colour on increasing the concentration of the acid added, it seems, however, that the reactions are often much more complicated.

Let us take as an example crystal violet. This is a basic dyestuff. Formula  $\{(\text{CH}_3)_2 \text{N} \cdot \text{C}_6\text{H}_2\}_2 \text{C} = \text{C}_6\text{H}_4 = \text{N}(\text{CH}_3)_2 \text{Cl}$ . In a neutral or faintly alkaline solution the colour is violet. On addition of acid the colour turns blue, then green and with still

TABLE 20.

Name of dye.	Distribution in neutral solution	Distribution in acid solution	Distribution in alkaline solution
<i>Methylene blue</i> (basic dyestuff).	Both layers about equally blue.	Same as in neutral solution.	All in the upper layer. The colour slowly changes to mauve.
<i>Crystal-violet</i> (basic dyestuff).	Much more in the alcohol layer. Both layers violet.	More in the alcohol layer. This is violet, the aqueous layer green.	All in the alcohol layer. Colour violet.
<i>Chrysoidine</i> (basic dyestuff).	Alcohol layer dark yellow to brown. Bottom layer pale yellow.	Same as in neutral solution but the colour is more brownish.	All in the alcohol layer. Colour dark yellow.
<i>Fuchsine</i> (basic dyestuff).	More in the alcohol layer. Both layers red.	Most in the alcohol layer. Colour is much darker.	The colour vanishes.
" <i>Neufuchsin</i> " (basic dyestuff).	More in the alcohol layer. Both layers red.	Most in the alcohol layer. Colour red.	All dark brown in the upper layer.
<i>Erythrosine</i> (acid dyestuff).	About equal distribution. Alcohol layer more orange like, the aqueous layer more red.	All in the alcohol layer. Colour orange.	As in neutral solution.
" <i>Wasserblau bläulich</i> " I (acid dyestuff).	About equal distribution; both layers blue.	Much more in the alcohol layer, blue.	All in the alc. layer. Colour orange, afterwards colourless.
<i>Rose Bengale</i> (acid dyestuff).	Equal distribution. Alcohol layer yellowish brown, aqueous layer orange.	All in the alcohol layer; light brown.	Much more in the alcohol layer; red.
<i>Quinoline-yellow</i> (acid dyestuff).	Equal distribution; both layers yellow.	Much more in the alcohol layer; yellow.	Much more in the alcohol layer; yellow.
<i>Eosine</i> (acid dyestuff).	About equal distribution.	All in the alcohol layer; yellow.	As in neutral solution.
<i>Roccelline</i> (acid dyestuff).	Both layers red.	All in the alcohol layer; red.	Both layers red but much darker than in neutral solution.
<i>Patent blue</i> (acid dyestuff).	Most in the alcohol; both layers blue.	Upper layer darker, aqueous layer more greenish.	All in the aqueous layer. Dark blue.
<i>Crystal-ponceau</i> (acid dyestuff).	Little in the alcohol layer; aqueous layers red.	Much more in the alcohol layer.	Little in the alcohol layer; aqueous layer more brownish.
<i>Congo-red</i> (substantive dyestuff).	Both layers red.	Blue deposit on the plane of demarcation.	All in the alcohol layer; red.
<i>Alkali blue 6 R.</i> Forms a colloidal solution in water, but little coloured, reddish blue and opalescent.	Alcohol layer dark blue; aqueous solution colourless.	As in neutral solution. Aqueous layer somewhat tinged.	All in the alcohol layer with slight reddish colour.
" <i>Indulin spritlöslich</i> " In water an almost colourless colloidal solution.	All with blue colour in the alcohol layer; aqueous layer colourless.	Nearly all in the alcohol layer, blue; aqueous layer somewhat tinged.	All with violet colour in the alcohol layer; aqueous layer colourless.

more acid yellow. From these solutions, however, it always passes into the alcohol layer with a violet colour. The only explanation we can give is this, that the dye adds an H-ion to its 3-valent N-atoms. These additive products might then be blue, green, or yellow, the non-dissociated salt, however, violet. In the alcohol layer the H-ion concentration is much less than in the aqueous layer and so these additive products are formed with more difficulty. By a large excess of HCl the upper layer turns green also. The green solutions also regain their violet colour by strong dilution: the added hydrogen ions are again split off by dilution.

“Patent blue” exhibits a similar behaviour; a very little acid causes the concentration in the alcohol layer to increase, on addition of more acid it again decreases, while the aqueous layer turns first green and afterwards yellow. When the aqueous layer is already yellow, the alcohol layer is still green.

The influence of acid and base was investigated quantitatively with methylene blue, quinoline-yellow and fuchsine.

From table 1, 2 and 3; 6—7; 14, 15 and 16 we notice that with a large excess of acid or base the course of the division curve is quite analogous to that in the neutral solution.

The influence of increasing quantities of acid or base is shown in the following table where in the first column is indicated the number of equivalents of acid or base in solution with one equivalent of colouring matter. The total quantity of dyestuff taken was always the same.

T A B L E 21.

Methylene blue <i>D</i> with	$c_w$	$c_{alc.}$	$c_a : c_w$
very much acid	130	140	1.08
8 eq. acid	140	120	0.86
4 " "	160	80	0.50
2 " "	170	70	0.41
1 " "	170	70	0.41
neutral	170	70	0.41
0.8 eq. KOH	170	70	0.41
2.6 " " .	150	86	0.57
6.2 " "	128	160	1.25
10 " "	90	300	3.33

If now we compare the distribution of dyestuffs between water and alcohol with that between water and fibres or other absorbents it appears that:

1. As in the case of the colour absorption by fibrous matters, the so-called adsorption-equation in which  $\frac{1}{n} < 1$ , also applies to the distribution between water and alcohol.

2. Addition of a base to the solution of basic dyestuffs and of an acid to acid dyestuffs strongly promotes the absorption by fibrous matter<sup>1)</sup> as well as the entry into the alcohol layer.

3. Wool and silk dyed with basic dyestuffs in which the base only has been retained are very readily decolourised by extraction with alcohol. The solubility of the free base, which in water is slight, is large in the fibre and also in the alcohol<sup>2)</sup>.

4. According to LOSEV<sup>3)</sup> no dyestuff is absorbed by paper fibre from a solution of crystal-violet when this substance is dissolved in butyl alcohol, amyl alcohol, aniline, chloroform or anisaldehyde; the absorption is perceptible from a solution in nitrobenzene, anisol, ethyl malonate or amyl nitrite and strong from the aqueous solution.

If now, we observe the distribution of this dyestuff between water and those solvents it appears that with the first group of solvents it practically disappears from the aqueous layer and that with the second group it distributes itself somewhat evenly over the two layers.

Nitrobenzene makes the only exception as it removes nearly all the dye from water although, according to LOSEV, no colouring matter is absorbed from it by paper.

This behaviour is now quite comprehensible if we look upon dyeing as being tantamount to *dissolving* the colouring matter in the fibre. For crystal-violet the fibre is a good solvent and water a bad one; the organic solvents of the first group are good, those of the second group are bad solvents. In the distribution of the dyestuff over the fibre and the organic solvent, less dyestuff will be absorbed in the fibre and more will be retained in the solvent, according to the greater solubility of the dyestuff in the latter. The division coefficient

$\frac{\text{fibre}}{\text{org. solvent}}$  will be the quotient of that between  $\frac{\text{fibre}}{\text{water}}$  and  $\frac{\text{org. solvent}}{\text{water}}$ .

5. FREUNDLICH and LOSEV have found that the order of adsorption is independent of the nature of the adsorption medium. With carbon

<sup>1)</sup> See i.a. PELET-JOLIVET, Koll. Zeitschr. 2, 225 (1908).

<sup>2)</sup> FREUNDLICH and LOSEV, loc. cit. p. 303.

<sup>3)</sup> LOSEV, Inaug. Dissert. p. 64.

as well as with silk, wool, cotton and cellulose the order of the three following dyestuffs was: crystal-violet, "neufuchsin", patent blue.

The same order, however, is noticed in the distribution of these dyestuffs between water and alcohol. Here again is shown the great analogy between the absorption of the dyestuff in fibres and the transition of the colouring matter into another solvent, which leads to the assumption that the absorbed dyestuff is present as a solid solution in the fibre.

We, therefore, conclude that the dye absorption in fibres is mainly a phenomenon of solid solution and that the assumption of a surface adsorption is in many cases unnecessary and should, therefore, be discarded.

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**Mathematics.** — "*On loci, congruences and focal systems deduced from a twisted cubic and a twisted biquadratic curve*". I.

By Prof. HENDRIK DE VRIES.

(Communicated in the meeting of September 28, 1912).

1. In the Proceedings of the Meeting of this Academy on Saturday Sept. 30, 1911, p. 259, Mr. JAN DE VRIES has investigated the locus of the points sending to three pairs of straight lines crossing each other three complanar transversals, and in the Proceedings of the Meeting of Nov. 25, 1911, p. 495, Mr. P. H. SCHOUTE has made the same investigation for the points sending to  $(n+2)_2$  pairs of straight lines crossing each other  $(n+2)_2$  transversals lying on a cone of order  $n$ . In the following pages one of the three pairs of lines will be replaced by a twisted cubic, the two others by a quartic curve of the first kind. Through a point  $P$  one chord  $a$  of  $k^3$  passes and two chords  $b$  of  $k^4$  pass; we ask after the locus of the points  $P$  for which the line  $a$  and the two lines  $b$  lie in *one* plane.

We imagine a chord  $a$  of  $k^3$ . Through an arbitrary point  $P$  of this chord pass two chords  $b_1, b_1^*$  of  $k^4$  and in the plane  $ab_1$  lies one chord  $b_2$  which does not meet  $b_1$  on  $k^4$  itself, in  $ab_1^*$  one such-like chord  $b_2^*$ ; if for convenience sake we call the points of intersection of  $b_2$  and  $b_2^*$  with  $a$  both  $Q$ , then in this way to each point  $P$  two points  $Q$  correspond. However, it is clear that to each point  $Q$  also two points  $P$  correspond, so that on  $a$  a (2,2) correspondence arises with four coincidences, and for these it is evident that the triplet  $a+2b$  is complanar. However, it is easy to see

that the four coincidences coincide two by two; for, if we call one of the two chords  $b$  through such a point  $b_1$ , then the other is  $b_2$ , but if we call the latter  $b_1^*$ , then  $b_1 \equiv b_2^*$ , so that really the coincidences coincide two by two. Furthermore it is easy to point out that in general the two coincidences do not fall in the points of intersection of  $a$  and  $k^3$ ; for, both chords  $b$  through such a point will in general not lie with  $a$  in *one* plane.

So out of these considerations follows that  $a$  intersects the demanded locus outside  $k^3$  in two more points; *if therefore we point out that  $k^3$  is a nodal curve, then we have proved that the demanded locus is a surface  $\Omega^6$  of order 6.* Now through a point  $P$  of  $k^3$  pass two chords  $b$  and in the plane through these lie two chords  $a$ ; so each point of  $k^3$  is a nodal point for the surface.

2. We again determine the order of  $\Omega^6$  by considering a chord  $b_1$  of  $k^4$ . Through a point  $P$  of  $b_1$  passes one  $a$  and in the plane  $ab_1$  lies one  $b_2$ ; if the latter intersects  $b_1$  in  $Q$  then to each point  $P$  one point  $Q$  corresponds. Inversely through  $Q$  passes one  $b_2$ , but in the plane  $b_1b_2$  lie three chords  $a$ ; so on  $b_1$  we find now a (1,3) correspondence with four coincidences, and these do not coincide two by two. For, through each coincidence passes one  $a$  and one  $b$ , but of course these cannot be exchanged. Neither does a single coincidence fall on  $k^4$ ; for through a point of intersection  $P$  of  $b$ , and  $k^4$  passes one  $a$  and the line connecting the two remaining points of intersection of plane  $ab_1$  and  $k^4$  does of course in general not pass through  $P$ . So a chord of  $k^4$  cuts  $\Omega^6$  outside  $k^4$  in four points more; *therefore  $k^4$  is for  $\Omega^6$  a single curve.*

This last result has something unexpected, for if we regard  $k^4$  by itself we arrive at quite a different result. Through a point  $P$  of  $k^4$  passes one  $a$  and in an *arbitrary* plane through this lie three chords  $b$  through  $P$ ; so that each point of  $k^4$  regarded by itself satisfies the given question an infinite number of times; if however we also take into consideration the points outside  $k^3$ , then we find according to the above mentioned a surface  $\Omega^6$  for which  $k^4$  is only a single curve.

That  $k^4$  is just a single curve is made clearer by the following consideration. The curve  $k^4$  is the section of two quadratic surfaces  $\Phi_1, \Phi_2$ , and the plane of the two chords  $b_1, b_2$  is at the same time the plane through  $P$  and the line of intersection  $s$  of the two polar planes  $\pi_1, \pi_2$ , of  $P$  with respect to  $\Phi_1$  and  $\Phi_2$ ; if now  $P$  falls exactly on  $k^4$ , then  $\pi_1, \pi_2$  become tangential planes in  $P$  to  $\Phi_1, \Phi_2$ , so their line of intersection  $s$  becomes the tangent  $t$  in  $P$  to  $k^4$ ; among all the planes through  $P$  only those through  $t$  come into consideration,



and as now the plane through  $t$  and the chord  $a$  through  $P$  is determined unequivocally, and as in this plane only two chords  $b$  lie, point  $P$  counts only once.

3. Through  $k^4$  pass four quadratic cones whose vertices we shall call  $T_1 \dots T_4$ . These vertices too behave themselves somewhat irregularly with respect to the question put originally, for an arbitrary plane e.g. through the line  $a$  passing through  $T_1$  contains always two chords  $b$ , so that also the four vertices of the cones regarded by themselves satisfy the given question an infinite number of times; *nevertheless these points are for  $\Omega^5$  only single points.*

This can be proved most easily with the aid of the edges of the tetrahedron  $T_1 \dots T_4$ . Let us consider e.g.  $T_1 T_2$  and let us regard  $k^4$  as the intersection of the two cones having  $T_1$  and  $T_2$  as vertices. All points  $P$  of  $T_1 T_2$  have with respect to the first cone only one polar plane  $\pi_1$ , viz. the plane  $T_1 T_3 T_4$ , and likewise with respect to the second cone only one polar plane  $\pi_2$ , viz.  $T_2 T_3 T_4$ ; the line of intersection  $T_3 T_4$  is therefore the line  $s$  for all points  $P$  of  $T_1 T_2$ , or in other words the planes  $Ps$  (or  $Pb_1 b_2$ ) for all points of  $T_1 T_2$  form a pencil of planes around the edge  $T_3 T_4$ . The question is to find the points  $P$  of  $T_1 T_2$ , for which the chord  $a$  of  $k^3$  passing through  $P$  lies in the plane  $Ps$  and to this end we have but to intersect each plane  $Ps$  by  $k^3$ , by means of which we find in each suchlike plane three chords  $a$  forming altogether a scroll  $\Omega^4$  of order four with  $k^3$  as a nodal curve and  $s$  as a single directrix. For, through a point of  $s$  only one chord  $a$  passes, whilst in a plane through  $s$  three of suchlike chords are lying, and through a point of  $k^3$  evidently two chords  $a$  pass intersecting  $s$ . Now this scroll  $\Omega^4$  intersects  $T_1 T_2$  in four points, but to these  $T_1$  and  $T_2$  themselves do not belong, because no reason whatever can be given why of the three chords  $a$  in the plane  $T_1 T_3 T_4$  e.g. just one should pass through  $T_1$ ; so we find on  $T_1 T_2$  four points of intersection besides the two vertices of the cones, and as the latter of course likewise belong to the surface they count once on  $T_1 T_2$  and therefore likewise in general.

If we determine the points of intersection of  $\Omega^6$  with the chord  $a$  through  $T_1$ , then we find that the two points which this chord has outside  $k^3$  in common with the surface (§ 1) coincide with  $T_1$ , which with a view to the preceding means that  $a$  touches the surface in  $T_1$ . We endeavour also to acquire on this special chord  $a$  the (2,2) correspondence of § 1, which is easily done and where we have but this to remark, that in the plane  $b_1 b_2$  as well as in the plane  $b_1^* b_2^*$  the four points of  $k^4$  lie two by two on two lines through  $T_1$ . If

now the point of intersection  $P$  of  $b_1$  and  $a$  is to coincide with the point of intersection  $Q$  of  $b_2$  and  $a$  then the four points of  $k^4$  in the plane  $ab_1b_2$  must form a complete quadrangle with  $P$  and  $T_1$  as two of the three diagonal points, and this is only possible if the line  $T_1P$ , thus  $a$ , lies on a special cone of order two, which will in general not be the case. In an arbitrary plane through  $T_1$  lie namely four points of  $k^4$ , forming a complete quadrangle; one of the three diagonal points is  $T_1$ , the two other ones lie in  $T_2T_3T_4$  and evidently describe here when the plane varies a conic through  $T_2, T_3, T_4$ . If now  $a$  happened to lie on the cone projecting this conic out of  $T_1$ , then two coincidences of the (2,2) correspondence would lie on the conic and the two others in  $T_1$ ; in every other case however all four coincidences must coincide in  $T_1$ , and so  $a$  must touch the surface  $\Omega^6$  in  $T_1$ .

4. We now proceed to determine the points of intersection of  $\Omega^6$  with an entirely arbitrary line  $l$ . To that end we allow a point  $P$  to travel along the line  $l$  and we investigate how often the chord  $a$  passing through  $P$  lies in plane  $Ps$ . According to § 3 the chords  $a$  issuing from the points  $P$  of  $l$  form a scroll of order four with nodal curve  $k^3$  and single directrix  $l$ ; the lines  $s$  belonging to the points  $P$  of  $l$  form a regulus and the planes  $Ps$  envelope a developable of class 3. If namely point  $P$  describes the line  $l$  then the two polar planes  $\pi_1$  and  $\pi_2$  of  $P$  with respect to  $\Phi_1$  and  $\Phi_2$  (comp. § 2) revolve around the two lines  $l_1, l_2$  conjugated to  $l_1$  and crossing each other in general; thus the line  $s$  describes a regulus with  $l_1$  and  $l_2$  as bearers.

Now the surface enveloped by the planes  $Ps$ . We imagine an arbitrary point  $O$  in space, we choose a point  $P$  on  $l$ , we determine the corresponding line  $s$  and we find the point of intersection  $Q$  of the plane  $Os$  with  $l$ ; in this manner to each point  $P$  one point  $Q$  corresponds. If reversely we wish to know how many points  $P$  correspond to  $Q$ , we draw the line connecting  $O$  and  $Q$  and we intersect it by the regulus of the lines  $s$  just found; through each of the two points of intersection passes one line  $s$  whose corresponding point  $P$  lies on  $l$ , so that to one point  $Q$  two points  $P$  correspond. Between the points  $P$  and  $Q$  on  $l$  there exists a (1, 2) correspondence; for the three coincidences the plane  $Ps$  passes through  $O$ ; so the planes  $Ps$  belonging to the points of a line  $l$  envelope a developable of class three.

We now add to the figure an arbitrary plane  $a$  and we determine the section of this plane with the scroll of order four, formed by

the chords of  $k^3$  resting on  $l$ , as well as with the developable just found of class three; the former is a rational curve of order four with three nodes in the points of intersection of  $\alpha$  and  $k^3$  and a single point in the point of intersection of  $\alpha$  and  $l$ , the second a rational curve of class 3 with a double tangent.

Through an arbitrary point of the curve of order four passes one chord  $a$ , intersecting  $l$  in  $P$ , and through  $P$  passes one plane  $Ps$ , so that in this way to each point of the curve  $k^4$  of order four one tangent of the curve  $k_3$  of class three corresponds, whilst in the same way we can see that to a node of  $k^4$  two different tangents of  $k_3$  correspond. In the same easy way we can convince ourselves that to each tangent of  $k_3$  one point of  $k^4$  corresponds and to the double tangent two different ones; so the result is that there exists a (1, 1) correspondence between the points of  $k^4$  and the tangents of  $k_3$ ; the question now is how many coincidences this correspondence possesses.

Let us take a point  $P$  on  $k^4$  and let us determine the corresponding tangent  $t$  of  $k_3$ , cutting  $k^4$  in four points  $Q$ ; reversely through one point  $Q$  pass three tangents  $t$ , and to each of these one point  $P$  corresponds; so between the points  $P$  and  $Q$  exists a (3, 4) correspondence and, as the bearer is rational, the number of coincidences is seven. One of these must necessarily be the point of intersection of  $l$  and  $\alpha$ ; for, through this point taken as point  $P$  of  $l$ , passes a chord  $a$  and likewise a plane  $Ps$  cutting  $\alpha$  of course according to a line passing through  $P$ , however without it being necessary for  $a$  to lie in the plane  $Ps$ . So we have here a coincidence in the plane  $\alpha$  to which no incidence of  $a$  into the plane  $Ps$  corresponds; if we set this case apart six coincidences remain which are each the consequence of a point of intersection of  $l$  and  $\Omega^6$ .

For the sake of completeness we add to the preceding that the regulus of the rays  $s$  belonging to the points  $P$  of  $l$  contains the four vertices of the cones  $T_1, \dots, T_4$  (comp. § 3); for  $T_1$  has as polar plane with respect to  $\Phi_1$  as well as to  $\Phi_2$  the plane  $T_2T_3T_4$ , so inversely the two polar planes of the point of intersection of  $l$  with this plane pass through  $T_1$ , and so does therefore their line of intersection  $s$ .

The developable of the planes  $Ps$  is of class three, so through each point  $P$  of  $l$  itself three planes  $Ps$  must pass; indeed two rays  $s$  of the regulus cut  $l$  and to these two points  $P$  of  $l$  correspond; so through  $l$  pass two planes  $Ps$  and these must for each point of  $l$  be added to the plane passing through that point but not through  $l$ .

5. As we have seen before  $k^4$  is for the surface  $\Omega^6$  a single curve,  $k^3$  a nodal curve, and the surface cannot contain other nodal curves for, if a point  $O$  is to be a double point, then through this point either more than one chord  $a$  or more than two chords  $b$  must pass; the former is only possible for the points of  $k^3$ , the latter only for those of  $k^4$ , and these two curves we have already investigated. *On the other hand the surface contains a number of single lines crossing each other, as many as twenty; the chords of  $k^3$  namely form a congruence of rays (1,3), those of  $k^4$  one (2,6), and these congruences have according to the theorem of HALPHEN  $1 \cdot 2 + 3 \cdot 6 = 20$  rays in common. Through a point  $P$  of such a ray passes one chord  $a$ , one chord  $b$  coinciding with  $a$  and one chord  $b$  more; so it is a single point for  $\Omega^6$ . Two of these lines cannot possibly intersect each other outside  $k^3$ , for in that case two chords  $a$  would pass through one point, which is impossible; it is not impossible for them to intersect on  $k^3$ , but this requires a peculiar situation of  $k^3$  and  $k^4$  with respect to each other, which we will not presuppose.*

An arbitrary plane through one of the twenty lines cuts  $\Omega^6$  besides in this line still according to a curve of order five which has with the line in common its two points of intersection with  $k^3$  but not those with  $k^4$ , because the latter are but single points for the surface. However besides the two points of intersection on  $k^3$  the curve must have three points more in common with the line, in which points the indicated plane must therefore touch the surface; *so the surface  $\Omega^6$  possesses an infinite number of threefold tangential planes, which are arranged in twenty pencils of planes, around the twenty lines of the surface as axes.*

A surface of order 6 is determined by  $\frac{7 \cdot 8 \cdot 9}{1 \cdot 2 \cdot 3} - 1 = 83$  points or in general single conditions; we shall investigate for how many single conditions  $k^3$ ,  $k^4$ , and the twenty lines of the surface count. The curve  $k^3$  must be a nodal curve; so we try to construct a surface of order 6 having  $k^3$  as a nodal curve. In an arbitrary plane  $\alpha$  we assume eighteen points quite arbitrarily; we determine the three points of intersection of  $\alpha$  with  $k^3$ , and we construct a plane curve of order 6 having these last three points as double points and at the same time containing the 18 points above mentioned; as a double point counts for three single data and a curve of order 6 is determined by  $\frac{1}{2} \cdot 6 \cdot 9 = 27$  points, we have in  $\alpha$  just enough data to determine the curve of order six.

In a second plane  $\beta$  we assume arbitrarily only 12 points, and we add to these the six points of intersection with the curve

lying in  $\alpha$ ; then we can also find in  $\beta$  a curve of order 6 which must lie on the surface. Finally in a third plane  $\gamma$  we have now of course to assume arbitrarily only 6 points and then the surface is determined; for every arbitrary fourth plane cuts the three curves lying in  $\alpha, \beta, \gamma$  together in 18 single points, and  $k^3$  in three points which must be double points, by which the section of the surface to be constructed is determined. Besides  $k^3$  we therefore want  $18 + 12 + 6 = 36$  points to determine the surface; so the condition that  $k^3$  is a nodal curve is equivalent to  $83 - 36 = 47$  single conditions.

If  $k^4$  is to lie on the surface of order six, then we have to take care that it must have twenty-five points in common with the surface; so  $k^3$  as a double curve and  $k^4$  as a single curve absorb  $47 + 25 = 72$  single conditions, so that but  $83 - 72 = 11$  conditions are left. Now a common chord of  $k^3$  and  $k^4$  has with every surface of order six passing twice through  $k^3$  and once through  $k^4$  in its points of intersection with both curves exactly six points in common with this; thus by distributing the eleven points which are left among eleven of the twenty common chords, we can be sure that also these eleven chords will come to lie on the surface. However, we know that on our surface  $\Omega^6$  all the twenty common chords lie; so we can state the following theorem: *the twenty common chords of  $k^3$  and  $k^4$  lie on a surface  $\Omega^6$  of order 6 passing twice through  $k^3$  and once through  $k^4$ ; it is the locus of all the points of space for which the triplet of chords  $a + 2b$  is complanar.*

6. The first polar surface of an arbitrary point  $O$  of space with respect to  $\Omega^6$  is a surface  $\Pi_1^5$  of order five passing once through  $k^3$ ; the complete section with  $\Omega^6$ , which must be of order thirty, breaks up into  $k^3$  counted twice and a residual section  $r^{24}$  of order twenty-four, from which ensues immediately that *the apparent circuit of  $\Omega^6$  out of an arbitrary point of space on an arbitrary plane is a curve of order twenty-four.*

The curve  $r^{24}$  has as is easy to see twelve points in common with  $k^3$ . The second polar surface of  $O$ , viz. a surface  $\Pi_2^4$  of order four, does not contain  $k^3$ , so it intersects it in twelve points; these are the points which  $k^3$  and  $r^{24}$  have in common. If namely we connect  $O$  with an arbitrary point  $P$  of  $r^{24}$ , then  $OP$  is a tangent in  $P$  of  $\Omega^6$ ; now if  $P$  lies on  $k^3$  then  $OP$  touches in  $P$  one of the sheets of  $\Omega^6$  passing through  $k^3$ , but in consequence of this on the line  $OP$  lie united in  $P$  three points of  $\Omega^6$ , and therefore two of  $\Pi_1$ , and one of  $\Pi_2$ . Each of these twelve points counts for three coinciding points of intersection of  $\Omega^6$  with its two polar surfaces; for, if we intersect

$k^3 + r^{24}$ , the section of  $\Omega^6$  and  $\Pi_1$ , by  $\Pi_2$ , then every point of intersection with  $k^3$  counts for two, with  $r^{24}$  for one; therefore each of the twelve points under discussion counts for three. As the complete number of points of intersection of the three surfaces is  $6.5.4 = 120$ , outside  $k^3$  there are  $120 - 3.12 = 84$ . It is wellknown that the tangents in these points to  $r^{24}$  pass through  $O$ : *thus the apparent circuit of  $\Omega^6$  possesses eighty-four cusps.*

To determine the class of  $\Omega^6$  and with it of the circumscribed cone, resp. the apparent circuit, we assume a second point  $O'$ , and we construct the first polar surface  $\Pi_1'$ ; this, too, passes through  $k^3$  and intersects the curve  $r^{24}$  just found in 120 points of which twelve however lie on  $k^3$ , and count singly, because  $r^{24}$  is a single section of  $\Omega^6$  and  $\Pi_1$ , and  $k^3$  is again a single curve of  $\Pi_1$ ; so outside  $k^3$  the three surfaces have  $120 - 12 = 108$  points in common, *so that the class of  $\Omega^6$  amounts to 108.*

By applying the PLÜCKER formula  $v = \mu(\mu - 1) - 2\delta - 3\alpha$  to the apparent circuit, we find

$$2\delta = \mu(\mu - 1) - v - 3\alpha = 24 \cdot 23 - 108 - 3 \cdot 84$$

or

$$\delta = 96.$$

*The projecting cone out of  $O$  contains therefore 96 double edges, the apparent circuit 96 nodal points.*

The PLÜCKER equation dualistically related:

$$\mu = v(v - 1) - 2\tau - 3\iota,$$

applied to the apparent circuit furnishes us with

$$2\tau + 3\iota = v(v - 1) - \mu = 108 \cdot 107 - 24 = 11532,$$

whilst the third formula:  $\iota - \alpha = 3(v - \mu)$  furnishes for  $\iota$

$$\iota = 84 + 3(108 - 24) = 336;$$

so we find  $2\tau = 11532 - 3 \cdot 336 = 10524$ , or  $\tau = 5262$ .

Now however we have to remember that the planes through  $O$  and the twenty lines of  $\Omega^6$  are threefold tangential planes of the cone, that their traces are therefore threefold tangents of the apparent circuit and that therefore they count together for sixty double tangents. If we subtract these from the entire number 5262, *then for the apparent circuit remain 5202 real double tangents completed by 20 threefold ones.*

A cusp in the apparent circuit is generated by a principal tangent (a tangent with contact in three points) of the surface passing through  $O$ ; these principal tangents form a congruence, of which according to the above mentioned the first characteristic (number of rays through a point) is eighty-four. The second characteristic indicates the number

of rays in a plane; in order to find this we have but to determine the number of inflexions of a plane section of  $\Omega^6$ . We have already seen that this plane section is of order 6 and of class 24, and that it contains 3 double points, whilst the number of cusps is 0; from this ensues easily that the number of inflexions is 54, the number of double tangents 192; *the congruence of the principal tangents of  $\Omega^6$  has therefore the characteristics 84 and 54, those of the double tangents 5202 and 192.*

7. Through each point  $P$  of  $\Omega^6$  passes a plane  $\pi$ , in which are situated one chord  $a$  of  $k^3$  and two chords  $b$  of  $k^4$ ; we wish to study the surface which is enveloped by those planes  $\pi$ . The class of this surface can be determined in different ways; we shall deduce this number in the first place by asking how many planes  $\pi$  pass through a chord  $a$  of  $k^3$ . Through the point of intersection  $A_1$  of  $a$  with  $k^3$  passes one plane  $\pi$  which in general however does not pass through  $a$ , and the same holds for the second point of intersection  $A_2$ . Besides these two points  $a$  has still but 2 points  $S_1, S_2$  in common with  $\Omega^6$ , and through *these* passes a plane  $\pi$  containing  $a$ ; for  $S_1$  e.g. is a point of  $\Omega^6$  exactly for this reason that the chord  $a$  lies with two chords  $b$  of  $k^4$  in a plane  $\pi$ . So to each of the two points  $S_1, S_2$  a plane  $\pi$  through  $a$  corresponds.

However planes  $\pi$  can also pass through  $a$  without it being necessary for the point of intersection  $P$  of the triplet  $a + 2b$  to lie exactly on  $a$  itself. If we make a plane  $\alpha$  to rotate round  $a$ , it contains in each position 2 more chords  $a$  and 6 chords  $b$ , forming a complete quadrangle. The two chords  $a$  describe the two quadratic cones by which  $k^3$  is projected out of the two points  $A_1, A_2$ , the diagonal points of the complete quadrangle describe a twisted curve possessing in each plane  $\alpha$  three points apart from the points lying on  $a$  itself and which are nothing but  $S_1, S_2$ ; so the diagonal points form a twisted curve  $k^5$  of order 5 resting in 2 points  $S_1, S_2$  on  $a$ , (and containing evidently the four vertices  $T_1, \dots, T_4$ , § 3). Let us consider a point of intersection of this  $k^5$  with one of the just mentioned quadratic cones, we then have evidently obtained a point of  $\Omega^6$  and at the same time a plane  $\pi$  through  $a$ . Now  $k^5$  intersects each cone in ten points, but among these are  $S_1$  and  $S_2$ ; so outside  $a$  lie only sixteen points of intersection and if we again add  $S_1$  and  $S_2$ , counted once, we then find *that the surface enveloped by the planes  $\pi$  bearing a triplet  $a + 2b$  is of class eighteen.* We shall indicate it by  $\Omega_{18}$ .

As easily we can determine the class of  $\Omega_{18}$  by means of a chord

$b$  of  $k^4$ . If it cuts  $k^4$  in  $B_1, B_2$ , we must bear in mind that these points according to § 2 are for the surface  $\Omega^6$  single points only, from which ensues that through those points only one plane  $\pi$  passes which comes in consideration if we make, as is done here, a point  $P$  to describe the surface and if we ask after the surface to be enveloped by the planes  $\pi$ ; this one plane however does not pass in general through  $b$ . Besides  $B_1, B_2$   $b$  has with  $\Omega^6$  four more points  $S$  in common; through each of these evidently passes a plane  $\pi$  containing  $b$ .

However, there are of course now again planes  $\pi$  through  $b$ , whilst point  $P$  lies outside  $b$ . A plane  $\beta$  through  $b$  contains three chords  $a$  and these describe when  $\beta$  rotates round  $b$  a scroll of order four with  $k^3$  as a nodal curve and  $b$  as a single directrix (§ 3). The plane  $\beta$  contains moreover 6 chords of  $k^4$ , of which however one coincides with  $b$ , so that one diagonal point lies on  $b$  and two outside  $b$ . These describe when  $\beta$  rotates round  $b$  a twisted curve of order four, resting in  $B_1, B_2$  on  $b$ ; if namely  $\beta$  touches  $k^4$  in  $B_1$  or  $B_2$ , it is easy to see that one of the two diagonal points lying in general outside  $b$  coincides with the point of contact. This curve of order four intersects the just mentioned scroll of order four in sixteen points, to which however belong  $B_1$  and  $B_2$  as these lie in  $b$  and therefore on the scroll too; if we set these aside, because they do not satisfy the question, fourteen are left, and these added to the four points on  $b$ , which do satisfy the question, give us again the number 18.

We can also determine by the way followed here the eighteen tangential planes of  $\Omega_{18}$  through an entirely arbitrary line  $l$ . The chords of  $k^3$  resting on  $l$  lie again on a surface of order four, and the diagonal points of the complete quadrangles in the planes  $\lambda$  through  $l$  lie on a curve of order five resting in two points on  $l$ ; for, the chord  $a$  of  $k^3$  which we discussed above is for  $k^4$  an arbitrary line, so it contains as many diagonal points as in the general case. The curve and the surface intersect each other now in twenty points, but to these belong the two points of intersection of the curve with  $l$ , which do not satisfy the question; so there are again eighteen left.

8. An arbitrary plane through one of the twenty common chords of  $k^3$  and  $k^4$  contains beside this chord, representing an  $a$  as well as a  $b$ , one chord  $b$  more, cutting the other outside  $k^4$ , and therefore it is a plane  $\pi$  to be counted once; so through each of the twenty chords pass an infinite number of tangential planes of  $\Omega_{18}$ , from



which ensues that *the twenty common chords of  $k^3$  and  $k^4$  are single lines of  $\Omega_{18}$ .*

The plane  $\pi$  issuing from a point of  $k^3$  contains two chords  $a$  and so it counts twice as tangential plane of  $\Omega_{18}$ , whilst reversely it is easy to see that  $\Omega_{18}$  can have no other double tangential planes than these; for, in such a plane must either lie two chords  $a$ , which leads to the curve  $k^3$ , or more than two chords  $l$ , which is the case for the points of  $k^4$ , but as for the latter only the plane through the tangent and the chord  $a$  comes into consideration (§ 2), the last possibility disappears and only the points of  $k^3$  are left. *The double tangential planes of  $\Omega_{18}$  are therefore the planes  $\pi$  corresponding to the points of  $k^3$ ; they envelope a developable  $\Delta_9$  of class 9.*

In order to find this number we look for all the double tangential planes passing through an arbitrary point  $B_1$  of  $k^4$ . Such a plane then must contain a chord of  $k^4$  passing through  $B_1$  intersecting  $k^3$ , and it can thus be obtained for instance by intersecting  $k^3$  by the cubic cone projecting  $k^4$  out of  $B_1$ , which furnishes 9 points of intersection, or inversely by intersecting  $k^4$  by the cubic cone projecting  $k^3$  out of the vertex  $B_1$ , which furnishes 12 points of intersection, of which three however coincide with  $B_1$  and must be taken apart. If now we call  $A$  such a point of intersection lying on  $k^3$  then really through this point passes one double tangential plane of  $\Omega_{18}$  containing point  $B_1$ ; so the class of the developable is nine.

Through a point  $A$  of  $k^3$  pass likewise 9 tangential planes of  $\Delta_9$ ; for one of these points  $A$  itself is the point from which start the two chords  $b$  of  $k^4$ , in the eight other planes on the other hand the chords  $b$  start from an other point; from this ensues that through  $A$  pass altogether ten chords of  $k^4$  which start from the point of  $k^3$  and which at the same time lie in the tangential planes of  $\Delta_9$  corresponding to those points; *the locus of those chords is a surface  $\Omega^{20}$  of order twenty for which  $k^3$  is a tenfold curve.*

For, an arbitrary chord of  $k^3$  meets in each of its 2 points of intersection with  $k^3$  ten generatrices of the scroll to be found, and is intersected outside  $k^3$  by no chords of  $k^3$ .

In a tangential plane of  $\Delta_9$  lie also two chords  $b$  intersecting  $k^3$ , viz. in point  $A$  to which that tangential plane corresponds; let us also ask after the locus of these chords  $b$ . Through each point of  $k^3$  pass two, through each point of  $k^4$  nine, because (see above) the cubic cone projecting  $k^4$  out of that point is intersected by  $k^3$  in nine points; let us now determine the points of intersection of the scroll to be found with a chord  $b_1$  of  $k^4$ , then of these in each of the two points of intersection of  $b_1$  with  $k^4$  lie nine united. If further-

more we make a plane  $\beta$  to rotate round  $b_1$  then the chord  $b_2$  in that plane, which cuts  $b_1$  outside  $k^4$ , describes a scroll having six points in common with  $k^3$ ; through each of these passes a chord  $b_2$  which cuts  $k^3$  and  $b_1$ ; *the scroll to be found is therefore a surface  $\Omega^{24}$  of order  $2 \times 9 + 6 = 24$ . It has  $k^3$  as a nodal curve and  $k^4$  as a ninefold curve.*

9. The surface  $\Omega^{20}$  found in the preceding § possesses no other manifold curve than  $k^3$ . Each scroll of order  $n$  contains namely a nodal curve which is cut by a generatrix in  $n-2$  points, because a plane through a generatrix contains as residual section a curve of order  $n-1$ , and of the  $n-1$  points of intersection of this curve with the generatrix only one acts as a point of contact, so that all the remaining ones are due to a nodal curve. Now a plane through a generatrix of  $\Omega^{20}$  contains a residual section of order nineteen with two ninefold points on  $k^3$ ; these together form eighteen points of intersection of the generatrix with the nodal curve, so that the latter is complete with  $k^3$  only. *On the other hand the surface contains twenty double generatrices, viz. the common chords of  $k^3$  and  $k^4$ , as is easy to see, and these same lines are double generatrices of  $\Omega^{24}$ .*

The surface  $\Omega^{24}$  contains besides the nodal curve  $k^3$  and the ninefold curve  $k^4$  still a new nodal curve which is cut by each generatrix in five points: for, a plane through a generatrix contains a residual section of order twenty-three with two eightfold points on  $k^4$  and a single point on  $k^3$ , forming together seventeen points; so the generatrix must contain five points more of an other nodal curve. And indeed, if we make a plane to rotate round a generatrix  $b_1$ , it then possesses in each position still one chord  $b_2$  of  $k^4$  not meeting  $b_1$  on  $k^4$ ; this chord describes a regulus intersected by  $k^3$  in six points, of which one however coincides with the point of intersection of  $b_1$  and  $k^3$ ; through the remaining five passes every time one generatrix of  $\Omega^{24}$  meeting  $b_1$  outside  $k^3$  and  $k^4$ , thus in a point of the new nodal curve.

We can find the order of this new nodal curve with the help of the theory of the permanency of the number. We conjugate an arbitrary generatrix of  $\Omega^{24}$  which we call  $g$  to all others which shall then be called  $h$ , and in this way we find  $\infty^2$  pairs of lines  $gh$  to which we will apply in the first place SCHUBERT'S formula:

$$\varepsilon\sigma = 2 \cdot \varepsilon\beta - 2 \cdot \varepsilon g^1).$$

The letter  $\varepsilon$  indicates the condition that two rays  $g$  and  $h$  of a

1) SCHUBERT: "Kalkül der abz. Geom.", p. 60, N<sup>o</sup>. 22.

pair lie at infinitesimal distance without intersecting each other,  $\sigma$  on the other hand indicates that they intersect each other without coinciding; the combination  $\varepsilon\sigma$  therefore indicates the number of pairs the two components of which lie at infinitesimal distance and cut each other at the same time. This can take place in our case as follows. We know that the double tangential planes of  $k^4$  are simply the tangential planes of the four quadratic cones cutting each other in  $k^4$ ;  $k^3$  has with these four cones twenty-four points in common and through such a point pass evidently two generatrices satisfying the condition  $\varepsilon\sigma$  and forming together one pair satisfying this condition. *These generatrices are the torsal lines of  $\Omega^{24}$  and their points of intersection with  $k^3$  are the cusps.* The surface  $\Omega^{24}$  contains however also twenty double generatrices, viz. the common chords of  $k^3$  and  $k^4$ , and these too must evidently be regarded as satisfying the indicated condition; the number  $\varepsilon\sigma$  is therefore  $= 20 + 24 = 44$ .

The symbol  $\varepsilon g$  indicates the number of pairs of rays which coincide and where  $g$  (or  $h$ , which is of course the same) intersects a given line; now that given line intersects the surface in twenty-four points: so  $\varepsilon g$  is twenty-four. We thus find:

$$2 \cdot \varepsilon\beta = \varepsilon\sigma + 2 \cdot \varepsilon g = 44 + 48 = 92,$$

so

$$\varepsilon\beta = 46.$$

The symbol  $\beta$  indicates the condition that the two rays of a pair intersect a ray of a given pencil, thus the symbol  $\varepsilon\beta$  indicates the condition that those two rays lie moreover at infinitesimal distance without intersecting each other; so the quantity  $\varepsilon\beta$  indicates in our case evidently exactly the class of a plane section of  $\Omega^{24}$ . If now we remember that such a section contains in general no cusps, we then find for the number of double points:

$$2\delta = 24 \cdot 23 - 46 = 552 - 46 = 506,$$

so:

$$\delta = 253.$$

Now we know of these 253 double points the following: 1. the three points of intersection with  $k^3$ ; 2. the four points of intersection with  $k^4$ , each of which is a ninefold point and therefore absorbs  $\frac{1}{2} \cdot 9 \cdot 8 = 36$  double points; 3. the points of intersection with the twenty double generatrices, so together  $3 + 4 \cdot 36 + 20 = 167$ ; *the order of the new nodal curve is therefore  $253 - 167 = 86$ .*

A plane curve of order twenty-four can possess at most  $\frac{1}{2} \cdot 23 \cdot 22 = 253$  double points, just the number of our case:  $\Omega^{24}$  is therefore a rational surface.

We control this result by using a second formula of SCHUBERT viz <sup>1)</sup>.

$$\sigma p + \varepsilon g + \varepsilon \beta = g_p + gh + h_p,$$

where  $\sigma p$  indicates the number of pairs whose components without lying at infinitesimal distance intersect each other, whilst the point of intersection lies in a given plane, thus evidently in our case the order of the complete nodal curve, however taken twice, because each ray can be a  $g$  as well as an  $h$ , and therefore each pair of rays satisfying the condition  $\sigma p$  counts for two pairs;  $g_p$  designates the number of pairs where the line  $g$  passes through a given point, a number which is evidently zero in our case, because all our rays belong to a surface and can therefore not pass through a point taken arbitrarily; for the same reason we find  $h_p$  zero. On the other hand  $gh$  designates the number of pairs where  $g$  intersects a given line  $l_1$  and  $h$  a given line  $l_2$ , a number which in our case evidently amounts to  $24 \cdot 24 = 576$ , because  $l_1$  is intersected by twenty-four generatrices  $g$ ,  $l_2$  by twenty-four generatrices  $h$ , and each line of one group can be joined to each of the other. As  $\varepsilon g = 24$ ,  $\varepsilon \beta = 46$ ,  $\sigma p$  becomes  $576 - 24 - 46 = 506$ , and as the order of the nodal curve is half of it, we find back the quantity 253.

In the formula:

$$\sigma e + \varepsilon g + \varepsilon \beta = g_e + gh + h_e, \text{ } ^2)$$

which is dualistically opposite to the last but one,  $\sigma e$  indicates the number of pairs of rays whose components intersect each other and whose plane passes through a given point. Now, too, each pair we find is counted double, because each ray can be  $g$  as well as  $h$ ; so  $\frac{1}{2}\sigma e$  is the class of the developable, enveloped by the double tangential planes of  $\Omega^{24}$ . The quantity  $g_e$  indicates the number of pairs where the ray  $g$  lies in a given plane, and  $h_e$  indicates the same for  $h$ ; both numbers are in our case evidently zero; and from this ensues  $\sigma e = \sigma p = 506$ , so that the class of the doubly circumscribed developable of  $\Omega^{24}$  amounts to 253.

For the sake of completeness we shall discuss in short the surface formed by the chords of  $k^3$  resting on  $k^4$ . Through any point of  $k^4$  passes one, so that  $k^4$  is a single curve: through any point of  $k^3$  on the other hand eight pass, because the quadratic cone projecting  $k^3$  out of that point is intersected by  $k^4$  in eight points; so  $k^3$  is an eightfold curve. From this ensues again that an arbitrary chord

<sup>1)</sup> l.c. p. 60, N<sup>o</sup>. 23.

<sup>2)</sup> l.c. p. 60, N<sup>o</sup>. 24.

of  $k^3$  intersects the demanded surface in each of its two supporting points with  $k^3$  in eight points and no more; because two chords of  $k^3$  cannot intersect each other outside  $k^3$ ; *the demanded surface is thus of order sixteen, and it has  $k^3$  as an eightfold curve,  $k^4$  as a single curve.* That  $k^3$  is the only manifold curve follows again out of the circumstance that two chords of  $k^3$  can meet each other only on the curve itself; *on the other hand the twenty common chords of  $k^3$  and  $k^4$  are again double generatrices.* As an eightfold point counts for  $\frac{1}{2} \cdot 8 \cdot 7 = 28$  double points, the complete number of double points of a plane section is  $3 \cdot 28 + 20 = 104$ ; a plane curve of order sixteen can however contain at most  $\frac{1}{2} \cdot 15 \cdot 14 = 105$  double points; *so the surface is of genus 1.*

10. Through a point  $P$  of space pass two chords  $b$  of  $k^4$  situated in the plane  $\pi$  through  $P$  and the line of intersection  $s$  of the two polar planes of  $P$  with respect to the two quadratic surfaces  $\Phi_1, \Phi_2$  (§ 2) intersecting each other in  $k^4$ ; we shall conjugate this plane  $\pi$  as focal plane to  $P$  and we shall discuss the focal system that is formed in this way. *Each point of space has then one focal plane (so  $\alpha = 1$ ), with the exception of the points of  $k^4$  having  $\infty^1$  focal planes, viz. all the planes containing the tangent in that point.*

In order to find inversely the number  $\beta$  of the foci  $P$  of an arbitrary plane  $\pi$ , we intersect that plane with  $\Phi_1$  and  $\Phi_2$ ; this gives rise to two conics  $k_1^2, k_2^2$ , and with respect to these we take the polar lines  $p_1, p_2$  of an arbitrary point  $P$  of  $\pi$ . The polar planes of  $P$  with respect to  $\Phi_1, \Phi_2$  then pass through  $p_1, p_2$  and the line  $s$  conjugated to  $P$  contains the point of intersection of  $p_1$  and  $p_2$ ; if  $s$  is thus to be situated in plane  $\pi$ , then  $p_1$  and  $p_2$  must coincide, and this takes place only for the vertices of the polar triangle which  $k_1^2$  and  $k_2^2$  have in common; *so  $\beta$  is  $= 3$ .*

The third characteristic quantity,  $\gamma$ ), indicating how often a focus  $P$  lies on a given line, whilst at the same time the focal plane  $\pi$  passes through that line, is found as follows. When  $P$  describes the line  $l$  the two polar planes rotate round the two lines  $l_1, l_2$  conjugated to  $l$  with respect to  $\Phi_1, \Phi_2$ ; their line of intersection  $s$  describes a regulus with  $l_1, l_2$  as bearers, and passing through the vertices of the four doubly projecting cones of  $k^4$ ; this regulus intersects  $l$  in 2 points, through which every time one line  $s$  passes, and the foci conjugated to these lines lie on  $l$  as is in fact the case for all lines  $s$  of the regulus; for these two foci however the focal plane  $\pi = Ps$  passes through  $l$ ; *so  $\gamma = 2$ .*

1) STURM, "Liniengeometrie" I, p. 78.

Through the points  $P$  of space the polar planes  $\pi_1, \pi_2$  with respect to  $\Phi_1, \Phi_2$  are conjugated one by one to each other; so we can regard the lines  $s$  as the lines of intersection of conjugated planes of two collinear spaces, and we then find immediately *that the lines  $s$  form*<sup>1)</sup> *a tetrahedral complex, for which the tetrahedron of the four vertices of the cones of  $k^3$  is the surface of singularity*, in such a sense that each arbitrary ray through one of the vertices or in one of the faces of that tetrahedron is a complex ray, whilst in general the tetrahedral complex being quadratic a point has but a quadratic complex cone, a plane a quadratic complex curve. As namely the two polar planes of the vertex of a cone coincide in the opposite face of the tetrahedron, each line in this face can be regarded as a ray  $s$ , and as of a line  $l$  through  $T_1$  e. g. the two conjugated lines lie in  $T_2T_3T_4$ , inversely the two polar planes of the point of intersection of those conjugated lines pass through  $l$ , so that  $l$  is a complex ray  $s$ . The complex cone of a point  $P$  in  $T_2T_3T_4 = \tau_1$  breaks up into two pencils, one with vertex  $P$  and lying in  $\tau_1$ , the other with vertex  $P$  and lying in a certain plane through  $P$  and  $T_1$ ; and likewise the complex curve in a plane through  $T_1$  degenerates into 2 points, viz.  $T_1$  itself and a certain point in the line of intersection of that plane and  $\tau$ .

A ray  $s$  being the line of intersection of the polar planes  $\pi_1, \pi_2$  of a certain point  $P$  with respect to  $\Phi_1, \Phi_2$ , inversely through an arbitrary ray  $s$  two planes  $\pi_1, \pi_2$  must pass having the same pole  $P$ ; if however a line lies in a plane, then the conjugated line passes through the pole of that plane; thus for  $s$  the two conjugated lines  $s_1, s_2$  must pass through  $P$  and must intersect each other in  $P$ ; *so we can also define the rays  $s$  as those rays of space whose two conjugated lines with respect to  $\Phi_1, \Phi_2$  intersect each other*. In this we have also a means to determine the focus of an arbitrary ray  $s$ ; we have but to find the point of intersection of  $s_1$  and  $s_2$ .

The rays  $s$  conjugated to the points of an arbitrary line  $l$  form a regulus as we have seen above; those conjugated to the points of a ray  $s$  must thus form according to the preceding a quadratic cone, and this is evidently the complex cone for the focus  $P$  of  $s$ , by means of which a construction for that cone has been found; we take the ray  $s$  conjugated to  $P$ , we allow a point to describe that ray and we determine for each position the two polar planes; the line of intersection of these describes the complex cone when the point describes the ray  $s$ . Just as the regulus for a line  $l$ , so each complex cone contains the vertices of the four doubly projecting cones;

<sup>1)</sup> STURM l. c. p. 342.

and as the two conjugated lines of a ray  $s$  lie likewise on the complex cone of the focus  $P$ , they themselves are again rays  $s$ .

The complex curve lying in a plane  $\alpha$  we find by regarding the two poles  $A_1$  and  $A_2$  of  $\alpha$ . The conjugated lines  $l_1, l_2$  of the lines  $l$  of  $\alpha$  pass respectively through  $A_1$  and  $A_2$ , and are conjugated by the rays  $l$  one by one to each other, so that two projective nets of rays are formed; the locus of the points of intersection of rays conjugated to each other is a twisted cubic through  $A_1$  and  $A_2$ , and furthermore through the four vertices of the cones  $T_1 \dots T_4$ ; for, the two conjugated lines of the line of intersection of  $\alpha$  with  $T_2 T_3 T_4$  are  $A_1 T_1, A_2 T_1$ . The rays  $s$  conjugated to the points  $P$  of that twisted cubic as foci lie in  $\alpha$  and envelope the complex curve; and as each line of the plane  $T_2 T_3 T_4$  can be taken as a ray  $s$  conjugated to e.g.  $T_1$ , so also the line of intersection with  $\alpha$ , the complex conic will touch the four surfaces of the tetrahedron.

**Botany.** — “*On the demonstration of carotinoids in plants*” (First communication): *Separation of carotinoids in crystalline form.*  
By Prof. C. VAN WISSELINGH. (Communicated by Prof. MOLL).

(Communicated in the meeting of September 28, 1912).

Many of the chemical, physical, and microscopical investigations on the yellow and red colouring matters of the vegetable kingdom which are grouped under the name carotins<sup>1)</sup> or carotinoids<sup>2)</sup> bear witness to great care and originality. They have, however, not all led to similar results. Especially the microscopical investigation has led to very divergent results which sometimes seriously conflict with those obtained by chemical and physical means. The investigators might be divided into two groups; one is inclined to consider all carotinoids identical; believing that the differences observed are not of a chemical nature. The other group distinguishes several carotinoids.

T. TAMMES<sup>3)</sup> is especially a representative of the first group. After investigating a fairly large number of plants, she comes to the conclusion that the yellow to red colouring matter of plastids, in green, yellow variegated and etiolated leaves, in autumn leaves, in flowers, fruits and seeds, in diatoms, green, blue, brown and red

<sup>1)</sup> CZAPEK, *Biochemie der Pflanzen*, I. p. 172.

<sup>2)</sup> M. TSWETT, *Über den makro- und mikrochemischen Nachweis des Carotins*, *Ber. d. d. bot. Ges.* 29. Jahrg., Heft 9, 1911, p. 630.

<sup>3)</sup> T. TAMMES, *Über die Verbreitung des Carotins im Pflanzenreiche*, *Flora*, 1900, 87. Bd. 2. Heft, p. 244.

algae, completely agrees in chemical and physical properties with the carotin from the root of *Daucus Carota*.

The most recent macrochemical investigations of carotinoids, namely that by WILLSTÄTTER and his pupils have not confirmed TAMMES' results. WILLSTÄTTER and MIEG<sup>1)</sup> isolated two carotinoids from the leaves of the stinging nettle, namely, carotin ( $C_{40}H_{56}$ ) which substance was found to be identical with the carotin from the root of *Daucus Carota* and xanthophyll ( $C_{40}H_{56}O_2$ ), whilst WILLSTÄTTER and ESCHER<sup>2)</sup> obtain from tomatoes another carotinoid, lycopin ( $C_{40}H_{56}$ ) isomeric with *Daucus*-carotin. From two objects three different carotinoids were thus obtained, namely, two hydrocarbons and one oxygenated substance.

The great difference between the results of microscopical and macro-chemical investigations determined me to try various methods which have been recommended for the demonstration of carotinoids by microscopical means.

These methods are sometimes divided into direct and indirect ones. The direct ones depend on the addition of reagents which bring about colorations, such as, for example, the beautiful blue coloration with sulphuric acid; the indirect methods are based on the separation of the carotinoids in crystalline form in the cells or tissues. Only in a few cases do the carotinoids occur as crystals in the cells; generally they are combined with, or dissolved in a substance that is fluid, fatty and saponifiable by alkalies<sup>3)</sup>. This substance occurs in the plastids, or forms, as in the case of lower organisms, oily drops in the cells<sup>4)</sup>. The aim of the indirect methods is to free the carotinoids and to crystallize them out. The following methods belong to this category.

#### *Potash Method.*

This method invented by MOLISCH<sup>5)</sup> was used originally for the demonstration of xanthophyll or carotin in green leaves. Fresh leaves

<sup>1)</sup> R. WILLSTÄTTER, Untersuchungen über Chlorophyll, IV. RICHARD WILLSTÄTTER und WALTER MIEG, Über die gelben Begleiter des Chlorophylls, *Justus Liebig's Annalen der Chemie*, 355. Bd. 1907, p. 1.

<sup>2)</sup> RICHARD WILLSTÄTTER und HEINR. H. ESCHER, Über den Farbstoff der Tomate, *Hoppe-Seyler's Zeitschrift für Physiol. Chemie*, 64. Bd. 1910, p. 47.

<sup>3)</sup> F. G. KOHL, Untersuchungen über das Carotin und seine physiol. Bedeutung in der Pflanze, 1902, p. 118 et seq.

<sup>4)</sup> W. ZOPF, Zur Kenntnis der Färbungsursachen niederer Organismen. Erste Mitteilung, Beiträge zur Physiol. und Morphol. niederer Organismen, Erstes Heft, 1892, p. 35. Zweite Mitteilung, l. c. Zweites Heft, 1892, p. 5.

<sup>5)</sup> HANS MOLISCH, Die Krystallisation und der Nachweis des Xanthophylls (Carotins) im Blatte, *Ber. d. d. bot. Ges.* Bd. XIV, 1896, p. 19.



or parts of them are placed in alcoholic potash containing 40% by volume of alcohol and 20% by weight of potassium hydroxyde; they are left in the mixture for several days while light is excluded, until all the chlorophyll has been extracted. With green leaves the potash method gives good results, but also in many other cases, for example, with etiolated, autumn, and variegated leaves, flowers, fruits, algae, etc. We may assume that generally the carotinoids are separated in those cells in which they occur in the living plant. Sometimes the carotinoids wander and form aggregations of crystals in apparently arbitrary places or outside the objects. As a rule the method gives positive results; only in a few cases does it fail.

In order to obtain an idea of the way in which the crystal-formation takes place, I have in a few cases studied the effect of MOLISCH's reagent on the living material under the microscope. The crystallisation will be illustrated by a few examples.

Large yellow plastids are found in the corolla of *Calceolaria rugosa*. The carotinoid occurs dissolved in a substance, fluid and easily saponifiable, which forms a yellow peripheral layer in the plastids. On the addition of MOLISCH's reagent the plastids sometimes form yellow globules with a sharp edge, which quickly change into globules or masses which show a less well-defined contour and are products of saponification. Often saponification proceeds still more rapidly, so that globules with sharp outline are no longer seen, but the saponification-products appear immediately. They dissolve and out of the solution there grow in a few minutes orange-yellow acicular or narrow band-shaped crystals, often very long and strongly curved and sometimes fissured.

In the ligulate florets of *Gazania splendens* large orange-coloured plastids occur in which can be distinguished globules that are in constant movement. When MOLISCH's reagent is added they rapidly form orange balls with sharp outline. These arise out of the union of the globules described above. The phenomenon is not the result of saponification, as KOHL<sup>1)</sup> assumes, for warming in water or a stay in dilute spirit (70%) has the same effect. In my opinion it is caused by the cells dying and the plastids losing their structure. In *Gazania splendens* saponification of the globules formed proceeds very slowly. After being in MOLISCH's reagent for 20 days (in vitro), I saw only orange globules in the cells which were coloured dark-blue by sulphuric acid. When I investigated the flowers after 24 days, I again found many orange globules, but at the same time there

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<sup>1)</sup> F. G. KOHL, l. c. p. 122.

were also many well-formed crystals, orange crystal-plates with rounded ends and aggregates of the same crystal-plates. The crystals give the various colour-reactions of carotinoids and the same is the case with the orange globules, in proof, that all the carotinoid has not yet crystallized out.

The formation of crystals by the potash method is easily explained. In the living plant the carotinoids occur in solution. They are dissolved in a fluid, fatty substance. When MOLISCH'S reagent is added the plastids are destroyed and the fluid substance forms globules, which are coloured orange-yellow or orange by the carotinoid. MOLISCH'S reagent farther brings about saponification and solution. The oily substance is saponified and the cells are filled with a solution of the saponification-product in which the carotinoid is soluble. This solution is diluted by the reagent in which the objects are placed and the carotinoids, which are not soluble in MOLISCH'S reagent, separate in the cells.

By reason of the above facts, I assumed that the carotinoids must be soluble in soap-solutions. This was indeed found to be the case. If, for example, after being washed out with water, preparations, in which carotinoids occur in the form of crystals, are placed in soap-spirit (*Spiritus saponatus Pharm. Nederl. Ed IV* without oil of lavender) the crystals dissolve.

As is evident from the examples described above, the saponification of the fatty substance and the separation of crystals sometimes takes place rapidly and sometimes very slowly. According to the nature of the object minutes, hours, days, weeks, or months are required for the separation of the crystals. Among objects which require much patience are the following in addition to the ligulate florets of *Gazania splendens* those of *Hiëracium aurantiacum*, *Doronicum Pardalianches* and *Taraxacum officinale*, in which crystals were observed after 24, 48 and 74 days respectively. In the ligulate florets of *Hiëracium murorum* and *Inula Helenium* and in the petals of *Viola cornuta* no crystals were perceived after 60, 39 and 29 days respectively. That the carotinoids do not separate out in these last examples, must be attributed to the fact that the oily substance is not saponified and holds the carotinoid in solution. The yellow or orange-yellow globules, which are seen in the cells, are coloured blue by sulphuric acid, transient blue by bromine water and green by iodine in potassium iodide; this proves that the carotinoid is still present.

I do not think that the long continued action of MOLISCH'S reagent is accompanied by any disadvantage. I have no indication that the carotinoids are destroyed by it and often fine crystallisations are finally obtained. I have tried MOLISCH'S potash method in about 40 cases and

only in the 3 last-mentioned was there no crystallisation of carotinoid. It is however possible that in these cases also a still more prolonged action might have had the desired result.

TAMMES <sup>1)</sup> and KOHL <sup>2)</sup> maintain that all the crystals, which are obtained by the potash method consist of carotin, however they may differ in colour and shape. The colour would only depend on the thickness of the crystals and of the angle at which they are seen. BECKE <sup>3)</sup> however, considers as a result of crystallographic investigations that the crystals obtained by MOLISCH's method are not identical. I myself have come to the following conclusions. Before proceeding I wish to remark that the names of the colours which I use are in agreement with those of KLINCKSIECK et VALETTE's Code des Couleurs, 1908. Often the numbers, given to the colours in the book, have also been mentioned.

In many cases the crystals differ greatly in colour and shape. In general, with respect to the colours the crystals can be arranged in two groups, namely, orange-red and red (Kl. et V. 91, 76, 51, 46) to which the violet-red (Kl. et V. 581) of the fruit of *Solanum Lycopersicum* are allied and a second group composed of orange-yellow and orange crystals (Kl. et V. 176, 151, 126, 101). The colour is also influenced by the thickness of the crystals. Red is always present in the first group, but not in the second.

However different the shape of the crystals may be, it is still true that colour and form are often connected. Among the red crystals, as a rule well-developed plates are found which have the shape of small parallelograms and sometimes also of rhombs. Generally small plates are formed which are several times more long than broad or narrower ones which resemble pointed needles. The parallelograms and rhombs are often imperfect. Parts may be wanting, angles and sides may be rounded. Very often the red crystals form aggregates. The root of *Daucus carota* and the fruit of *Solanum Lycopersicum* belong to the objects in which carotinoids occur in the form of crystals. In *Daucus* the carotin has formed in addition to well-developed red parallelograms and rhombs all sorts of other crystals which are even curved band shaped. In the tomato lycopin is found in the form of red-violet needles.

The orange-yellow and orange crystals are also very varied. Especially in those cases in which the carotinoids crystallize out slowly, little plates of crystal are often found which are generally

<sup>1)</sup> l. c. p. 242, 244.

<sup>2)</sup> l. c. p. 33 et seq. and p. 67.

<sup>3)</sup> HANS MOLISCH, l. c. p. 24.

several times more long than broad, rarely about as long as broad. The ends are for the most part rounded, occasionally pointed, irregular or more or less straight. Often oval and whetstone-shaped crystals are found. Once they were seen as rhombs with rounded sides. In a few cases the crystals showed large surfaces of indefinite shape, in other cases the surfaces were narrow, long and slightly curved. The multifarious ribbon- and needle-shaped crystals that occur are allied to this last-mentioned form. These are generally much curved. Straight needles are rare. The ribbon-shaped crystals are often branched or split up into separate curved needles. Finally connected with the curved, needle-shaped crystals there are filamentous ones, which may be very much twisted and often form clews. The crystal plates often form aggregates.

When leaves are treated with MOLISCH'S reagent aggregates of crystals are generally formed in the cells which contain chlorophyll; they are composed of orange-yellow plates and red crystals resembling needles.

The shape of the orange-yellow and orange crystals often differs in one and the same object. In the flower of *Dendrobium thyrsiflorum* I found orange-yellow (Kl. et V. 151) whetstone-shaped plates and orange-yellow (151) thread-like crystals, also aggregates of fine needle-shaped crystals coloured bright orange (101) and to some extent orange-red (81). In the flower of *Cucurbita melanosperma* I found thread-like crystals and very thick, almost completely straight, flat needles in the hairs.

The shape of the crystals is sometimes very dependent on external circumstances, as for example, on the quantity of MOLISCH'S reagent into which the object is put. In the petals of *Chelidonium majus*, for example, I got thread-shaped crystals whenever I placed them in a flask with a large quantity of MOLISCH'S reagent, and crystal plates when a petal was placed in a small quantity of MOLISCH'S reagent between a cover-slip and a slide.

However diverse the crystals may be there is an important point of difference between the red and orange-red on the one hand and the orange-yellow and orange crystals on the other hand, namely, that when the carotinoids have separated out in the form of plates, among the former well-shaped parallelograms are nearly always formed and these are not met with among the orange-yellow and orange crystals.

In the leaves of *Urtica dioica* I was able to observe that the quantity of the reagent may influence not only the shape of the crystals but also the place where they are formed. By using much

of MOLISCH'S reagent a small aggregate of orange-yellow and red crystals appears in every cell; with little of the reagent I got large red and yellow aggregates of crystals in various places in the tissue or outside it. This last result need cause no surprise. The carotinoids are soluble in the solution of the saponification-products formed and not in MOLISCH'S reagent. When a small quantity of the reagent is used no quick dilution of the soap-solution occurs and the carotinoids will have the chance of changing their place in the tissue. In general it is therefore preferable not to use too small a quantity of the reagent, unless for any reason large aggregates of crystals are desired.

I have applied the potash method of MOLISCH to the following objects.

Flowers: *Trollius caucasicus* Stev., *Nuphar luteum* Sm., *Chelidonium majus* L., *Meconopsis cambrica* Vig., *Corydalis lutea* DC., *Erysimum Perofskianum* Fisch. et Mey., *Sinapis alba* L., *Isatis tinctoria* L., *Viola cornuta* L. var. *Daldowie Yellow*, *Cytisus sagittalis* Koch (*Genista sagittalis* L.), *Cytisus Laburnum* L., *Spartium junceum* L., *Thermopsis lanceolata* R. Br., *Cucurbita melanosperma* A.Br., *Ferula* sp., *Inula Helenium* L., *Doronicum Pardalianches* L., *Doronicum plantagineum* L. *excelsum*, *Calendula arvensis* L., *Taraxacum officinale* Wigg., *Hiëracium aurantiacum* L., *Hiëracium murorum* L., *Gazania splendens* Hort., *Asclepias curassavica* L., *Calceolaria rugosa* Hook., *Dendrobium thyrsiflorum* Rehb. fil., *Iris Pseudacorus* L., *Narcissus Pseudonarcissus* L., *Clivia miniata* Regel, *Tulipa hortensis* Gaertn., *Fritillaria imperialis* L., *Lilium croceum* Chaix, *Hemerocallis Middendorffii* Trautv. et Mey.

Green leaves: *Chelidonium majus* L., *Taraxacum officinale* Wigg., *Urtica dioica* L., *Triticum repens* L., *Selaginella Kraussiana* A.Br.

Yellow variegated leaves: *Sambucus nigra* L. fol. var., *Graptophyllum pictum* Griff., *Croton ovalifolius* Vahl.

Fruits: *Sorbus aucuparia* L., *Solanum Lycopersicum* Trn.

Root of *Daucus Carota* L.

Algae: *Cladophora* sp., *Spirogyra maxima* (Hass.) Wittr., *Haematococcus pluvialis* Flot.

It must be noted that in four of the above-named objects in their natural state carotinoids already occur in the form of crystals, namely in the root of *Daucus Carota*, the fruits of *Sorbus aucuparia* and of *Solanum Lycopersicum*, and in the flower of *Clivia miniata*.

#### *Acid method.*

By treating parts of green plants with dilute acids FRANK<sup>1)</sup> observed

<sup>1)</sup> A. TSCHIRCH, Untersuchungen über das Chlorophyll, Landwirtsch. Jahrbücher, XIII. Bd., 1884, p. 490. HANS MOLISCH, l.c. p. 26.

the formation of red or reddish yellow crystals, especially in the stomata. MOLISCH<sup>1)</sup> repeated the experiment with the leaves of *Elodea* and also observed such crystals which according to him, correspond to the crystals he obtained by his potash method. TAMMES<sup>2)</sup> experimented on a great number of plants and various parts of plants with dilute acids, as, for example, hydrochloric acid, oxalic acid, tartaric acid, chromic acid, picric acid, acetic acid, and hydrofluoric acid. Picric acid was used in a solution of alcohol, the other acids in aqueous solutions of various strengths. The investigation yielded positive results in the case of leaves, and other green parts of plants, flowers, green algae and Fucoideae. In all the cases investigated, over 30, crystals were obtained after some hours or days which, according to the above-mentioned writer, agreed completely with the crystals which had been obtained by the potash method and were found to consist of carotin. With yellow variegated, yellow autumn and etiolated leaves the experiment was without result, a fact which TAMMES<sup>3)</sup> is unable to explain.

When plants or parts of plants which contain chlorophyll are investigated with dilute acids allowance must be made for the action of the acids on the chlorophyll. When MOLISCH's reagent is used the chlorophyll dissolves with saponification of the ester, separation of phytol and formation of chlorophyllin potassium<sup>4)</sup>, but the action of acids on the chlorophyll produces insoluble derivatives. WILLSTÄTTER, who treated alcoholic extracts obtained in the cold from dried plants with acids, obtained, when the magnesium had been eliminated, phaeophytin<sup>5)</sup>, which like chlorophyll<sup>6)</sup> consists of two component parts, namely, phaeophytin a (phytylphaeophorbide a) and phaeophytine b (phytylphaeophorbide b). Earlier investigators also already

1) l. c. p. 26.

2) l. c. p. 216 et seq. and p. 242 et seq.

3) l. c. p. 220.

4) RICHARD WILLSTÄTTER, (Untersuchungen über Chlorophyll), II. Zur Kenntnis der Zusammensetzung des Chlorophylls, Justus Liebig's Annalen der Chemie, 350. Bd. 1906, p. 48.

RICHARD WILLSTÄTTER und FERDINAND HOCHEDER, III. Über die Einwirkung von Säuren und Alkalien auf Chlorophyll, l. c. Bd. 354, 1907, p. 205.

5) R. WILLSTÄTTER, II. Zur Kenntnis der Zusammensetzung des Chlorophylls, l. c. R. WILLSTÄTTER und F. HOCHEDER, l. c.

RICHARD WILLSTÄTTER und MAX ISLER, XX. Über die zwei Komponenten des Chlorophylls, l. c. Bd. 390, Heft 3, 1912, p. 269.

6) RICHARD WILLSTÄTTER und MAX UTZINGER, XVI. Über die ersten Umwandlungen des Chlorophylls, l. c. 382. Bd. p. 129.

R. WILLSTÄTTER und M. ISLER, l. c.

obtained products produced by the action of acids on chlorophyll. HOPPE-SEYLER <sup>1)</sup> obtained from grass by extraction with boiling alcohol a crystalline chlorophyll derivative, which he subjected to a number of operations in order to separate it from other substances and to purify it. He named it chlorophyllan. TSCHIRCH <sup>2)</sup> states that when parts of plants that contain chlorophyll are treated with acids, chlorophyllan crystallizes out in the cells. WILLSTÄTTER, ISLER, and HUG <sup>3)</sup> have after further investigation compared the chlorophyllan of HOPPE-SEYLER to phaeophytin. In the opinion of these investigators it is not a pure compound but chlorophyll more or less decomposed by plant acids and allomerised by treatment with solvents. For this reason they consider the name chlorophyllan unsuitable for the chlorophyll derivative obtained by means of acids.

TAMMES <sup>4)</sup> also discussed the action of acids on chlorophyll and comes to the conclusion that the formation of chlorophyllan offers no hindrance to the demonstration of carotin, because, although it must be admitted that the crystals obtained may perhaps be contaminated by some chlorophyllan, yet in the main they are composed of carotin. KOHL <sup>5)</sup> evidently agrees with TAMMES. He writes: "Mehr oder minder unbewusst ist die Säuremethode schon früher von einigen Forschern angewandt worden, unbewusst insofern, als das auskristallisierende Carotin irrtümlich für Chlorophyllan gehalten und nur in einzelnen Fällen als solches erkannt wurde." I consider TAMMES' reasoning inconclusive, whilst KOHL does not further explain his views. A simple investigation of the crystals shows that they are very different from carotin-crystals and there is even no reason to assume that they contain any carotin.

I exposed fresh plants and parts of plants containing chlorophyll to the action of acids at the ordinary temperature, oxalic acid from 1% to 10%, hydrochloric acid of 5%, tartaric acid of 10% and hydrofluoric acid of 2%. Without exception after a day crystals had separated out. They form small aggregates attached to the chromatophores. The crystal aggregates resemble spherical bodies, but with high magnification the constituent crystal plates can be distinguished. Only in one case, namely in *Cladophora*, did I see long whip-shaped crystals projecting from the crystal aggregates. The crystal aggregates are not yellow, orange yellow, or red, but brown. In acetone they

1) F. HOPPE-SEYLER, *Zeitschr. f. physiol. Chemie* 3, 1879, p. 339.

2) A. TSCHIRCH, *Untersuchungen über das Chlorophyll*, l. c. p. 441.

3) R. WILLSTÄTTER und M. ISLER, l. c. p. 287 et seq. and p. 337.

4) l. c. p. 217 and 218.

5) l. c. p. 47.

are easily soluble, slowly in glacial acetic acid. With concentrated or somewhat dilute sulphuric acid, for example 66 $\frac{1}{2}$ %, they are not coloured blue, but green (Kl. et V. 326). The colour never resembles the blue colour which the crystals of carotinoids assume with sulphuric acid, and which never shows a green, but sometimes a slightly violet tint. The green-coloured crystal aggregates are soluble in sulphuric acid. The brown crystal aggregates are also coloured green by concentrated hydrochloric acid (specific gravity = 1.19); afterwards they dissolve slowly. With concentrated nitric acid they are not, as is the case of carotinoids, temporarily coloured blue; they deliquesce and form globules, which when gently warmed, gradually become colourless and presumably consist of phytol. Nor do they, like carotinoids, become temporarily blue in bromine water; the brown colour at first remains unchanged. Towards caustic potash the brown aggregates of crystals also behave quite differently from the crystals of carotinoids; they are entirely soluble in it; they also are completely soluble in dilute alcoholic caustic potash, as, for example, in MOLISCH'S reagent, in which the crystals of carotinoids are of course insoluble. Since they leave nothing behind on solution there is no reason for thinking that they contain carotinoids.

The behaviour of the brown aggregates towards reagents shows that they are composed of a chlorophyll derivative. Phaeophytin<sup>1)</sup> gives the same reactions, and sometimes more or less clearly shows crystalline structure. TAMMES and KOHL have confused carotin with a chlorophyll derivative. TAMMES' drawing N<sup>o</sup>. 22 of *Elodea canadensis* in particular clearly shows that such a confusion has taken place. In each cell a number of brown, round crystal aggregates are figured attached to and on the chromatophores. The crystalline structure is not indicated in the figure, but is not always easily distinguished in the full cells. Besides these crystal aggregates, I found in many cells, though not in all, red aggregates of crystals which resemble carotin and which are coloured blue by concentrated or somewhat dilute sulphuric acid, namely of 76%. These crystal aggregates are however not figured by TAMMES, nor are they mentioned.

Now it is somewhat explicable why TAMMES<sup>2)</sup> obtained negative results with yellow variegated, yellow autumn and etiolated leaves. These objects or the yellow parts of them contain no chlorophyll and are therefore unable to produce brown crystal aggregates of a chlorophyll derivative. But this does not, however, clear up every-

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<sup>1)</sup> R. WILLSTÄTTER und F. HOCHEDER, l. c. p. 222 and 223.

<sup>2)</sup> l. c. p. 220.



thing. For the non-green leaves and the parts which are not green, yet contain substances which belong to the carotinoids. How is it that these were not found by TAMMES, whilst in other non-green parts of plants such as flowers, TAMMES obtained after some days in all the eight cases investigated well-formed crystals which with reagents showed the reactions proper to carotin. I am convinced by the use of MOLISCH'S reagent that carotinoids exist in the yellow parts of yellow variegated leaves. Sometimes I obtained separation of orange-yellow crystals, in other cases they were orange-yellow and red, but all gave the reaction proper to carotinoids. KOHL<sup>1)</sup>, with etiolated leaves, arrived at a different conclusion from that of TAMMES. I cannot refrain from remarking that KOHL does not always correctly reproduce the results of TAMMES, with whom he is in entire agreement. The following is quoted from TAMMES<sup>2)</sup>: Ich habe auch gelbbunte, herbstlich gelbe und etiolirte Blätter in verdünnte Säurelösungen gebracht, aber stets mit negativen Resultaten. And from KOHL<sup>3)</sup>: Durch die neueren Untersuchungen der etiolirten Pflanzen mit Säuren, welche T. TAMMES in grosser Zahl ausführte und welche ich, um in die unsicheren Anschauungen einige Klarheit zu bringen, planmässig fortgesetzt habe, ist es nun mit Sicherheit erwiesen, dass in allen etiolirten Pflanzenteilen, so weit sie gelb gefärbt, mit verdünnten Säuren Carotin-Krystalle zur Ausscheidung gebracht werden können.

I treated objects, both with and without chlorophyll, such as green and yellow variegated leaves, yellow, orange-yellow, and orange flowers, and algae, with dilute acids at the ordinary temperature; namely, with 1%, 2% and 10% oxalic acid, 1% and 5% hydrochloric acid, 10% tartaric acid and 2% hydrofluoric acid solutions. The treatment often lasted one or two months. The objects which were subjected to this investigation, were the same as those investigated by the potash method of MOLISCH.

In the case of green leaves I obtained with the dilute acids the above mentioned brown crystalline aggregates of a chlorophyll derivative which were formed in each cell containing chlorophyll, and here and there in the tissue red crystals, loose plates or aggregates. In the case of flowers, of which I investigated about 25, I generally obtained no crystals with dilute acids. Only in two cases was there a positive result, namely, in *Asclepias curassavica*, where red crystals separated and in *Calceolaria rugosa* where orange-

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1) l. c. p. 48.

2) l. c. p. 220.

3) l. c. p. 48.

yellow ones appeared. In one of the yellow variegated leaves, namely, of *Graptophyllum pictum* I obtained the separation of small orange-yellow crystals in the yellow portion of the leaf. The crystals which had separated behaved towards reagents and solvents exactly as did the corresponding crystals obtained by the potash method.

With regard to the investigation of flowers with dilute acids, TAMMES' <sup>1)</sup> results and mine differ. Whilst she obtained well formed crystals in all cases, I obtained them only exceptionally. Our investigations were however mostly concerned with different flowers. I propose if possible to examine with acids those flowers which have been studied by TAMMES, but not yet by myself, in order to reach greater certainty on this point of difference. Whatever the ultimate results, I nevertheless already venture to state, that the method of inducing crystallisation of the carotinoids in plants by means of acids cannot in general be recommended. Often the yellow carotinoids in particular do not crystallize. Red crystals very often form in the tissue but not in all cases in which they can be obtained by the use of the potash method. This is the case, for example, in the flowers of *Nuphar luteum*, *Isatis tinctoria*, *Cytisus Laburnum* and *Thermopsis lanceolata* as also in the peduncles of *Trollius caucasicus*. In these many orange-yellow and a few red crystals were obtained by MOLISCH's reagent, whilst in the flower of *Asclepias curassavica*, in which, as stated above, red crystals had been separated out by means of acids, MOLISCH's reagent produced many red as well as a few orange-yellow crystals. When the carotinoids which yield red crystals are present in great quantity, they can therefore be demonstrated by acids, but when they are present in small quantity, they escape observation.

Another drawback to the acid method is that the carotinoids which yield orange-yellow crystals are very liable to decompose. Continuous treatment with acids as is necessary with the acid method, often is very harmful and may lead to complete decomposition of the carotinoids. They are much more liable to decomposition by acids, while they are still in solution in the fatty substance of the plastids, than when they have been separated as crystals by some other method. According to HUSEMANN <sup>2)</sup> WACKENRODER pointed out this decomposition so far back as 1832. In the treatment with acids I have sometimes found decomposition to occur even in the first few days. The colour of the flowers becomes paler and the

<sup>1)</sup> l. c. p. 243.

<sup>2)</sup> A. HUSEMANN, Über Carotin und Hydrocarotin, Ann. der Chem. u. Pharm. Bd. CXVII, 1861, p. 200.

yellow or orange oily globules and masses, which have been formed in the cells and which contain the carotinoid, also lose more or less of their colour. Sulphuric acid then no longer colours them blue or much more feebly than at the beginning of the experiment. The carotinoid decomposes without crystallising out. This decomposition is easily confirmed in *Chelidonium majus*, *Narcissus Pseudonarcissus*, *Doronicum Pardalianches* and *Tulipa hortensis*, for instance.

#### *Resorcinol Method.*

TSWETT<sup>1)</sup> has described a method of crystallising the carotinoids from plants and parts of plants under the microscope. The objects are placed on the microscope slide in a concentrated solution of resorcinol, containing 10 to 12 parts of resorcinol in 10 parts of water. I have used this method in eight cases, namely, in the leaves of *Urtica dioica*, in the flowers of *Chelidonium majus*, *Erysimum Perofskianum*, *Gazania splendens*, *Calceolaria rugosa* and *Narcissus Pseudonarcissus*, in *Cladophora* sp. and in *Haematococcus pluvialis*. In five cases, namely, in *Urtica*, *Chelidonium*, *Calceolaria*, *Narcissus* and *Cladophora* crystals separated rather quickly. In *Chelidonium*, *Calceolaria* and *Cladophora* crystals appeared in the cells, in the other two cases in and around the preparations. *Erysimum*, *Gazania* and *Haematococcus* which had given positive results with the potash method, gave negative results with the resorcinol solution. In the case of *Haematococcus pluvialis* JACOBSEN<sup>2)</sup> was also unable to obtain separation of crystals.

The shape of the crystals differs greatly. When with MOLISCH's reagent red and orange-yellow crystals were obtained, crystals of the same colour were formed with TSWETT's reagent in those cases in which the experiment gave a positive result. With respect to reagents the crystals behave in the same way as the carotinoid crystals obtained by the potash method.

TSWETT<sup>3)</sup> has also pointed out the variation in the crystals and has shown in *Lamium* by his adsorption method that different chemical bodies are present, carotin and xanthophyll. It seems to me that TSWETT's method will be applicable with success to many cases.

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1) M. TSWETT, Über den makro- und mikrochemischen Nachweis des Carotins, Ber. d. d. bot. Ges. 29. Jahrg. Heft 9, 1911, p. 630.

2) H. C. JACOBSEN, Die Kulturbedingungen von *Haematococcus pluvialis*, Folia Microbiologica I, 1912, p. 25.

3) l. c.

*Other methods.*

KOHL<sup>1)</sup> has remarked that possibly other substances also might be used to bring about the crystallisation of carotin. He surmises that chloralhydrate might be used for the purpose and intends to investigate this possibility. When the solvent action of chloralhydrate upon the various constituents of cells is considered and it is seen that carotin crystals in contrast to those of xanthophyll are fairly resistant, then it is natural to suppose that chloralhydrate may offer a suitable means of separating carotin as crystals. I have experimented with the leaves of *Urtica dioica* in a concentrated aqueous solution (7 in 10) of chloralhydrate. We know from the investigations of WILLSTÄTTER and MIEG<sup>2)</sup> that these leaves contain carotin and xanthophyll. When I placed a small piece of the tissue containing chlorophyll in a solution of chloralhydrate and observed it under the microscope, I could soon detect changes in the chromatophores and the formation of a globule in each cell, which gradually dissolved and left behind a small aggregate of red carotin crystals. Orange-yellow crystals of xanthophyll were not separated. As was to be expected therefore the method is of no use for the separation of xanthophyll because decomposition takes place. I cannot moreover recommend it for the separation of carotin-crystals, because carotin is also attacked by chloralhydrate and small quantities therefore may escape observation.

According to WILLSTÄTTER and MIEG<sup>3)</sup> xanthophyll is "spielend löslich" in phenol. Having in mind the solubility of many substances in liquefied phenol and having confirmed the fact that carotin dissolves much more slowly than xanthophyll, it occurred to me to try liquefied phenol for the separation of carotin or allied carotinoids. I used two mixtures, one of 10 parts by weight of phenol in loose crystals and 1 part by weight of water, the other consisting of 3 parts by weight of phenol in loose crystals and 1 part by weight of glycerine. I prefer the latter mixture, because it mixes more quickly with the water contained in the objects. I examined the flowers of *Erysimum Perofskianum*, *Asclepias curassavica*, the leaves of *Urtica dioica* and the ligulate florets of *Taraxacum officinale*. With petals of *Erysimum Perofskianum* the potash method yielded no beautiful result, and the acid method a negative one. I placed parts of the petals in the above mixtures between a microscope slide and a cover-slip. Under the

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<sup>1)</sup> l. c. p. 124.

<sup>2)</sup> l. c. p. 10.

<sup>3)</sup> l. c.

microscope I saw that the brightly coloured orange-yellow plastids quickly formed orange-yellow globules; crystals soon appeared in these globules. While the globules dissolve the crystals remain behind. These are orange-red plates and aggregates which very slowly dissolve in the phenol mixtures. To investigate these, the preparations can be washed out successively with dilute alcohol (70 %) and with water. With reagents they give the reactions characteristic of carotinoids.

When parts of the flower of *Asclepias curassavica* are placed in the mixture of phenol and glycerine, there quickly appear in all the cells numerous light and dark red or orange-red (Kl. et V. 11, 46, 51, 71, 91) crystals, in the same way as in *Erysimum Perofskianum*, among which were many plates and aggregates. They do not dissolve in the phenol solution; at any rate after three days they were still unchanged. When investigated with reagents in the way indicated above, they show the reactions proper to carotinoids. In *Urtica dioica* orange-red (81) crystal aggregates are formed here and there in the tissue, which after three days are still present in the mixture of phenol and glycerine. In the ligulate florets of *Taraxacum officinale* yellow globules soon arise; in this case no crystals occur; the globules completely dissolve. Clearly in these four objects carotinoids occur, which differ greatly with respect to their solubility in a mixture of phenol and glycerine (3 to 1), and are either insoluble or dissolve slowly or readily. In the last case the carotinoids do not separate.

WILLSTÄTTER and MIEG<sup>1)</sup> have dealt with the question whether, in addition to carotin, xanthophyll is also present as such in the living plant and have answered it affirmatively. Both substances, can indeed be separated with simple solvents, carotin from dried leaves with petroleum ether, xanthophyll from alcoholic extracts of fresh leaves according to the "Entmischungsmethoden" of G. STOKES, G. KRAUS, H. C. SORBY and R. SACHSSE<sup>2)</sup>. It is therefore reasonable to assume that in some cases the use of simple solvents in which the carotinoids themselves are but little or not soluble, might lead to the crystallisation of these substances. In a few cases I have indeed succeeded in doing this.

With the ligulate florets of *Taraxacum officinale* and *Doronicum Pardalianches* I did at first not succeed in crystallising even a part of the carotinoid by means of the potash method. It remained in solution in the yellow or orange-yellow globules which had formed in the cells. When I had treated the ligulate florets for a very short time with absolute alcohol or a certain quantity with very

<sup>1)</sup> l. c. p. 10.

<sup>2)</sup> See WILLSTÄTTER und ISLER, l. c. p. 275 et seq.

little absolute alcohol, I ascertained, that the oily substance which retained the carotinoid, was dissolved and that part of the latter had separated more or less crystalline and gave the reactions characteristic of carotinoids. Direct treatment of the florets with absolute alcohol led to similar results. When the treatment with absolute alcohol is prolonged or when too much of it is taken, the carotinoid dissolves completely.

In a few cases I succeeded in obtaining even with dilute spirit the separation of carotinoids in crystalline form. After being placed for one day in 70 % spirit the corolla of *Calceolaria rugosa* was seen to contain orange-yellow crystals, loose plates and aggregates. The petals of *Chelidonium majus* when soaked for a month in 20 % spirit are found to contain not only orange-yellow and yellow drops and globules but also orange-yellow needle and thread-shaped crystals, some straight and some very much curved. They are often attached to the globules and give the impression of having grown out of them. In the flower of *Narcissus Pseudonarcissus* crystallisation of the carotinoid took place already after one day in 20 % spirit. Long continued treatment with dilute spirit may cause the complete decomposition of the carotinoid; this was already the case in *Narcissus Pseudonarcissus* after a few days.

Finally I wish to point out that on account of ARNAUD's<sup>1)</sup> investigations it must be assumed that the results sometimes depend greatly on the season of the year. ARNAUD found, for instance, that the leaves of the chestnut and the stinging nettle contain most carotin during the flowering time (May). I also found that the separation of crystals in one and the same species was not always the same. This was especially the case in *Cladophora*, in which treatment with MOLISCH's reagent sometimes resulted in the separation of many orange-yellow and a few red crystals, and at other times yielded many red and a few orange-yellow ones. It is desirable to point out this difference. When these experiments are repeated by other investigators it must be taken into account.

It must be admitted that the results of the above crystallisation experiments point strongly to the frequent occurrence of several distinct carotinoids in a plant. In a subsequent communication the behaviour of carotinoids with respect to reagents and solvents will be dealt with and the results of the direct and indirect methods will be summarised.

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<sup>1)</sup> A. ARNAUD, Recherches sur la carotine; son rôle physiol. probable dans la feuille. Compt. rend. CIX, 1889, 2, p. 911.

**Astronomy.** — “*Determination of the geographical latitude and longitude of Mecca and Jidda executed in 1910—’11.*” By Mr. N. SCHELTEMA. Part I. (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of May 25, 1912).

### I. *Introduction.*

Mecca as we know is the holy city and the meeting-place for Mohammedan believers. Yearly some 200.000 gather there from different parts of the world in order to make their pilgrimages and many of them stay there for a couple of years to gain a thorough knowledge of the doctrines of their religion.

From an economical and political point of view as well as for the history of religion Mecca is a place of great significance. Moreover it forms an important starting-point for the geography of the interior of Arabia. Hence it is not surprising that constant efforts have been made to obtain closer and the most accurate possible knowledge about this centre of the Islam; but great and peculiar difficulties are connected with these endeavours on account of the fact that entrance into the “holy domain” is strictly prohibited to non-Mohammedans. Only now and again a few Europeans succeeded in stealthily penetrating into it and spending there some time.

It is well known that among these stands first our compatriot the present professor Dr. C. SNOUCK HURGRONJE, who spent some eight months in Mecca and put down his exhaustive researches in his standardwork about this town. It stands to reason that my position as Consul of the Netherlands at Jidda, the harbour of Mecca, often brought me into contact with this scholar, and it was he who in the course of our talks drew my attention to the fact that so much scientific work might be done in the Hedjaz. In particular he pointed out that even the geographical position of Mecca was not accurately known and he raised the question if I might not supply this deficiency.

Others had succeeded in making fairly accurate plans of the town but its absolute position had not yet been determined with sufficient exactness. Lack of good instruments, which are not easily transportable and the necessity of taking care that no attention was drawn in the vicinity had generally prevented astronomical observations.

The only person by whom direct determinations of the latitude and the longitude of Mecca have been published is ALI BEY EL ABASSI, or at any rate the man who under that name travelled in many

oriental countries from 1803 to 1807 and in the latter year also visited Arabia and Mecca. His "Travels" were published in London in 1816<sup>1)</sup>. He made his astronomical observations with a reflecting-circle of 10 inch diameter with 4 verniers by Troughton and an achromatic telescope by Dollond of 2 $\frac{1}{2}$  feet, with the aid of two chronometers by Brooksbanks and Pennington (see Vol. 1, p. XVII, Vol. 2, p. IX). The latitudes were determined by meridian altitudes of the sun and stars, the longitudes by the transporting of chronometers, by lunar distances and by observations of eclipses of the satellites of Jupiter. Of his determination of the position of Mecca it is mentioned in particular that it was accomplished by means of altitudes of the sun and of lunar distances (2, 94)<sup>2)</sup>; in the meantime the chronometer by Brooksbanks had been broken, while probably shortly afterwards, that of Pennington was stolen at Mina in the neighbourhood of Mecca, so that the determinations of longitude could not be continued. ALI BEY'S results, especially his longitudes such as they have been published can only be of little accuracy. Taking, however, into account the good instruments he had at his disposal, it is probable that a renewed calculation might amend matters, but his original observations are not likely to have been preserved.

Besides from direct observations the position of Mecca might also be derived from that of Jidda by means of journeys between the two places with noted directions and distances, as the latter place has at present been accurately determined by the observations of the English hydrography. Of these itineraries HUBER'S<sup>3)</sup> seems to stand first; it has been accurately calculated and discussed by J. J. HESS. Yet HESS<sup>4)</sup> himself must attribute to his results for the longitude and latitude of Mecca mean errors of resp.  $\pm 3'.2$  and  $\pm 3'.8$ ,

So even after this last investigation the position of Mecca was very unsatisfactorily determined and Prof. SNOUCK HURGRONJE'S proposition to try and obtain greater accuracy attracted me greatly. In the summer of 1909 I therefore applied to the director of the Leyden observatory, Prof. E. F. VAN DE SANDE BAKHUYZEN, who was much

<sup>1)</sup> *Travels of ALI BEY in Morocco, Tripoli, Cyprus, Egypt, Arabia, Syria and Turkey between the years 1803 and 1807, written by himself.* London 1816 2 vols.

<sup>2)</sup> Erroneously J. J. HESS says in his *Geographische Lage Mekkas* that ALI BEY'S longitude of Mecca is based on eclipses of the satellites of Jupiter.

<sup>3)</sup> CHARLES HUBER, *Journal d'un voyage en Arabie.* Paris 1891.

<sup>4)</sup> J. J. HESS, *Die geographische Lage Mekkas und die Strasse von Gidda nach Mekka.* Freiburg 1900.



interested in my plans and kindly promised me help and advice. The execution of the work was now rendered possible and by the kind dispensation of His Excellency the Minister of Foreign Affairs, to whom I here respectfully render thanks, I received a royal commission to execute astronomical observations in the Hedjaz.

Let me say first of all in what way I intended to set about the proposed plan. As it was quite impossible for me to enter Mecca and make observations, the help would be asked of Mr. A. SALIM, Pupil-Secretary-Interpreter of the consulate. As a Mohammedan he was perfectly free in his movements within the holy domain and having finished the 5 years' course of the Secondary School at Batavia, he was sufficiently well-grounded to successfully make the astronomical observations. Let me add that Mr. SALIM showed an eager interest, when I communicated my plans to him.

According to the consultations with Prof. BAKHUYZEN a more detailed plan was now made out for the execution of the observations. For the determination of the latitude of Mecca circummeridian-altitudes of stars were to be observed and the same was to be done also at Jidda, partly for practice, partly for the examination of the instrument and of the employed method of observation and finally to mutually control the results obtained by the English hydrographers and by ourselves. Secondly the difference of longitude between Jidda and Mecca was to be determined by transporting some chronometers to and fro between the two places, if possible a couple of times, while during the stay in each place as many determinations of time as possible would be made by altitudes of stars in the east and in the west. All the observations at Mecca having to be accomplished by Mr. SALIM, also the corresponding determinations of time at Jidda wanted for the derivation of the difference of longitude were to be executed by him. All the observations were to be made with a small altazimuth.

First of all I now tried to use the rest of my furlough to practise making observations at the Leyden observatory. The exceedingly unfavourable summer of 1909 gave, however, only very rare opportunities for observations and so I had to leave again for Jidda at the end of July without having acquired sufficient skill in observing.

Consequently the observations I accomplished after my arrival at Jidda left much to be wished for in arrangement as well as in accuracy. Besides, other circumstances, among which an extremely busy time at the consulate, concurred in impeding the work. Owing to all this the material collected in the winter of 1909—10 has so little value that we can henceforth leave it out of account.

Fortunately the next year was in all respects more favourable for my enterprise. During my furlough in the summer of 1910 I again had the pleasure to work for three weeks at the observatory under the guidance of Prof. VAN DE SANDE BAKHUYZEN, and this time the heavens often gave an opportunity for observations. After my stay at Leyden I was moreover able to practise quite by myself for a few weeks in Gelderland with the instrument I had taken with me.

Under good prospects I therefore returned to Jidda towards autumn, and when early in November the greatest heat and also the busiest time at the consulate were over, I could begin regular observations and also Mr. SALIM could practise systematically under my supervision. Soon we were able to execute determinations of time and of latitude alternately on succeeding days. But now we met with another mischance. The chronometer employed for the observations began to accelerate very much and very irregularly and at last it stopped altogether (December 2). Since no observations could be made with any of my pocket-chronometers, the only thing left to do was to stop our observations until another box-chronometer could be forwarded from Leyden.

Owing to this ill luck and on account of the irregular connexion between Holland and Jidda, a delay was caused of more than six weeks. Not till the end of January 1911 could we resume the observations and with a view to the advanced time, it seemed best that they should further be done by Mr. SALIM alone.

Thanks to his ability and zeal the series of observations undertaken could be brought to a satisfactory result between January 25 and March 23 1911. During this time three journeys were made to Mecca. Before the first journey and after the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> the corrections of the chronometers were determined at Jidda on 23 nights and during the journeys 14 determinations of time were accomplished at Mecca. Besides, the latitude of Mecca was determined on 10 nights and that of Jidda on 13 nights, while for the last mentioned place already 7 determinations of latitude had been accomplished by the two of us in Nov.—Dec. 1910.

Finally, a journey from Mecca to Jidda made on foot by Mr. SALIM with the determination of distances and directions enabled him to make a map of the road between the two places.

As much as possible we calculated our observations ourselves, also to continually control our instruments, but of course the accurate calculation and the systematic derivation and discussion of the results could not take place until after my return to Holland.. These have

been done at the observatory at Leyden under the supervision of Prof. VAN DE SANDE BAKHUYZEN, who also investigated the best methods of combining the observations. The extensive calculations have been for far the greater part executed by Mr. H. W. HAMERSMA, late chief mate of the Royal Dutch Navy.

In this way results have been obtained for the geographical position of Mecca which certainly exceed in accuracy all that has been known up to this time and therefore I take the liberty to offer a paper on this subject to the Royal Academy of Sciences.

## II. *Instruments. Stations of observation.*

The instrument with which our observations were made was the universal-instrument Pistor and Martins N<sup>o</sup>. 905, belonging to the Technical University at Delft and kindly lent to me by Prof. HEUVELINK. The same instrument had formerly been employed by Mr. S. P. L'HONORÉ NABER of the Royal Dutch Navy for his observations for the demarcation between the republic of Liberia and French Congo.

The telescope of the instrument is at the end of the horizontal axis, while for the observation of small zenith-distances a reflecting prism can be brought before the ocular. The circles are read with verniers, the diameter of the vertical circle is 130 mm. and that of the objective is 28 mm. The value of a division of the level attached to the alidade-circle is about 8". During my first stay at Leyden the spider-lines were broken. They were replaced by two horizontal threads only, at about 6' distance from each other.

For a moment we had thought of employing instead the small universal instrument of the Leyden observatory, which has the same dimensions but is read with micrometer-microscopes. The consideration, however, that it is advisable in the damp and warm climate of Jidda to make as little use as possible of spider-threads especially of movable ones, made us give up this idea.

In the choice of the chronometers to be used, particular attention had to be paid to the peculiar circumstances attending the transport from Jidda to Mecca, which is done by camels, so that shocks cannot be altogether avoided. Moreover the road is far from safe; nearly every year a caravan is attacked and robbed by Beduins and it is therefore desirable not to take any conspicuous boxes. To carry these on foot would be altogether impossible. Discussing this point with Prof. VAN DE SANDE BAKHUYZEN and Mr. C. F. J. COSYN, Chief of the bureau of instruments of the Royal Navy, the latter drew our attention to the pocket-chronometers of Leroy, the so-called *chronomètres*-

torpilleurs. These had been used by Mr. NABER in the above mentioned observations and had proved very satisfactory (see his communication in *Marineblad*, vol. 24), while also at Mr. COSYN's bureau they had been found to go very regularly.

Through the kind permission of the Admiralty six of these watches have been lent to me, while the Home Office took the risks of their carriage to and in the Hedjaz. I here express my respectful thanks to their Excellencies the ministers.

In order to carry these six watches Mr. NABER had had a wooden box made with six pigeonholes, which was again to be packed into a leather bag to be carried knapsack-wise. This box and this bag we were allowed to employ, and transporting the watches in this way we could be pretty sure that they were free from disturbance.

The observations, however, could not be made directly on their very low ticks (5 per second) and therefore I had from the Leyden observatory the loan of a box chronometer by Cummins. As I have said before, however, this chronometer got out of order in Nov. 1910, and then Prof. BAKHUYZEN sent me another chronometer, by Dent, so that the greater part of our observations has been made with this one.

Finally my equipment contained an aneroid-barometer marked: Holosteric 7225 with an attached thermometer, a separate thermometer for the external temperature and a magnetic boussole. The correction of the barometer was determined at Leyden, through a comparison with the normal barometer of the observatory and was found to be  $-1^{\text{mm}}.5$  in Dec. 1909 and  $-2^{\text{mm}}.8$  in Aug. 1911. No dependence on the reading of the barometer was appreciable and so I corrected all my readings with  $-2^{\text{mm}}$ . As corrections of the attached thermometer and of the other one I found respectively  $+1^{\circ}.0$  and  $-0^{\circ}.5$ , which corrections have always been added.

In the beginning there was some difficulty in getting the universal instrument well stationed at Jidda. The observations could not be made in the open because that would have been very conspicuous and we should certainly have been molested by the population, while no doubt difficulties would have arisen with the Turkish authorities. A fairly large enclosure next to the consulate, which I had been thinking of, proved to be impracticable, since the outlook to the west was too far intercepted by the consulate.

So there was nothing else for it but to find a place on the roof of the consulate. This seemed to be easy, since here, as everywhere else, there was a flat roof offering sufficient room. Such a roof, however, rests on fairly thin beams over which matting is spread

covered with a layer of cement, so that it trembles when walked upon. Yet I succeeded in constructing a fairly stable mounting; near one of the corners of the roof on two walls that crossed each other and were raised a few centimeters over the roof, two heavy beams were laid and cemented down and on the top of these two thin beams were nailed on which the tripod of the instrument could be placed.

For further illustration see the picture on plate I. This shows that the tripod was made heavier by a big block of stone and we took care not to touch the supporting beams, although we had to adopt rather uncomfortable poses for some of the positions of the telescope. We soon got used to this, however, and the end was attained. We could now walk round the instrument, even stamping our feet, without causing the bubble of the level to move in the least. Afterwards Mr. SALIM arranged his station as Mecca in exactly the same way on the roof of a house rented by me.

The only thing sometimes preventing pleasant and quiet working was the noise in our neighbourhood. Regularly every evening at about 8 o'clock there was a musical performance by the Turkish military band at Jidda, and even more troublesome was the noise often occurring in the evenings in my neighbour's house and occasioned by an ice-machine making almost two turns per second. All we could do was to wait till quiet should return, although sometimes stars were lost in this way.

We had also made a point of determining, if possible every night, the zenithpoint of the instrument on a signal at some distance. This was done in order to continually control the mutual stability of the parts of the instrument, and also to facilitate the computation of the observations and to trace immediately eventual errors, e.g. in the reading of full degrees or in the employed star. At Jidda we used as signal a lantern with a circular hole placed on the roof of the sufficiently far off French consulate. At Mecca the observer used a black spot on the wall of a post situated on the Jebel Abu Kobeis a hill quite close to the town.

### *3. Value of the parts of the level. Zenithpoint of the instrument.*

The divisions of the alidade-level are numbered in such a way that if the reading of the bubble is too low, the reading of the verniers must be increased. The value of a division was measured a couple of times by displacing the alidade, the instrument being clamped.

In Oct. 1909 11 determinations in 9 days gave 1 d. =  $7''.85 \pm 0''.20$   
 in Oct. 1910—March 1911 15 determinations  
 in 12 days . . . . . 1 d. =  $8''.91 \pm 0''.19$   
 while all the determinations together would yield 1 d. =  $8''.46 \pm 0''.17$

Will it be better to use for our observations the value  $8''.91$  or  $8''.46$ ? Since  $8''.7$  had been actually used for the calculations, there did not seem to be any reason to change. The influence of an error in the value of a division on our final results is but small. A change in the adopted value by  $0''.5$  would alter the results for the latitude of Mecca and of Jidda with less than  $0''.2$ .

The zenithpoint was with a few exceptions determined every evening and each time for both the horizontal threads. In the following table have been collected the means of the two results together with their differences, i.e. the mutual distance of the threads. (See the table on p. 535).

For each period there have been added the means of the daily results; in forming these means we have left out of account Nov. 18 and 24, the results of which days are divergent.

From this table it appears that in each period the zenithpoints, determined on different evenings, mostly agree satisfactorily, but that after every journey the reading for the zenith has become a little higher. After the last journey back from Mecca it has considerably increased, with about  $4'.5$ , probably owing to a displacement of the level-tube with regard to the alidade. A few oscillations seem to appear in the thread-interval, while two very diverging results occur in Nov. 1910.

#### 4. *Determination of the geographical latitude of Jidda and of Mecca.*

Coming to the observations proper I will now first communicate the latitude determinations executed at Jidda and at Mecca and the results derived from these. For their reduction we must naturally know the corrections of the chronometer used, just as knowledge of the latitude is required for the reduction of the time determinations. I will, however leave the tables containing the chronometer-corrections till the next paragraph.

With a few exceptions each latitude determination consists in the observation of a northern and of a southern star, each in the two positions of the instrument. Every time two pointings were made, one on each of the two threads; the level was always read before and after the reading of the verniers.

## ZENITHPOINT DETERMINED ON THE SIGNAL.

	Mean zenithpoint	Thread- interval		Mean zenithpoint	Thread- interval
Observations 1910			3rd period Jidda		
SCHELTEMA					
Nov. 18	90° 12' 20"0	5' 13"7	Febr. 18	90° 12' 17"4	5' 56"1
" 23	8.1	56.9	" 20	18.8	49.3
" 25	7.2	51.3	" 22	4.9	44.8
" 28	16.7	56.4	Mean	90° 12' 13"7	5' 50"1
" 30	15.8	53.9	4th period Mecca		
Mean	90° 12' 11"9	5' 54"6	Febr. 24	90° 12' 16"4	6' 5"0
SALIM			" 25	16.2	4.1
Nov. 24	90° 11' 52"2	5' 18"1	" 26	16.7	13.6
" 26	69.9	41.2	" 27	18.6	12.9
" 29	54.1	39.6	Mean	90° 12' 17"0	6' 8"9
Mean	90° 12' 2"0	5' 40"4	5th period Jidda		
Observations 1911			March 2	90° 12' 21"4	5' 40"3
1st period Jidda			" 3	25.1	51.0
Jan. 23	90° 11' 53"7	5' 44"4	" 7	28.2	51.8
" 25	60.2	54.6	" 8	24.7	46.1
" 26	47.3	50.0	Mean	90° 12' 24"8	5' 47"3
" 28	58.0	49.7	6th period Mecca		
" 30	57.8	48.1	March 11	90° 12' 24"8	6' 9"2
" 31	55.8	39.4	" 12	31.9	11.3
Febr. 1	52.0	50.9	" 14	23.5	8.2
" 3	60.2	53.8	" 15	32.7	7.8
" 6	57.1	48.6	" 16	38.3	5.0
" 7	54.2	34.4	" 17	35.6	6.2
" 8	48.5	46.8	Mean	90° 12' 31"2	6' 7"9
" 12	56.8	51.0	7th period Jidda		
Mean	90° 11' 55"1	5' 47"6	March 19	90° 16' 53"4	5' 49"1
2nd period Mecca			" 20	67.0	52.5
Febr. 15	90° 12' 10"2	5' 52"5	" 21	49.6	70.0
" 16	17.0	61.4	" 23	55.6	64.8
Mean	90° 12' 13"6	5' 57"0	Mean	90° 16' 56"4	5' 59"1

In reducing the observations that value of the zenithpoint was used, which had been determined on the day itself. In the very rare cases that the signal had not been observed the zenithpoint has been derived from the determinations of preceding and subsequent days.

We have always tried to choose the two stars for one evening in such a way that their absolute zenith-distances would not be too great and almost equal, in order to practically eliminate from the result of each evening the flexure of the instrument and the systematic division-errors of the circle. We have been fairly successful in this and find :

		$z$	$z_N - z_S$	Mean ( $z_N - z_S$ )
Jidda	1 <sup>st</sup> series	37° to 56°	— 3° to + 4°	— 1°.5
„	2 <sup>nd</sup> „	10 „ 40	— 4 „ + 2	— 0 .4
Mecca		23 „ 44	— 7 „ + 2	— 2 .0

while one evening only the zenithdistance has exceeded 45°.

Both the chronometers employed in the observations (as well as the Leroy-watches) had been regulated after mean solar time, and so their readings, after having been corrected, had still to be reduced to sidereal time. In all our calculations account was taken of course of the variation of sidereal time at mean noon with the longitude.

The pointings were mostly arranged fairly symmetrically with regard to the meridian. The reduction to the meridian was computed with the aid of ALBRECHT's tables; the term dependent on  $\sin^4 \frac{1}{2} t$  has always been taken into account if it exceeded 0".05. The star-places were taken from the Nautical Almanac, and BESSEL's refraction was used.

Below I shall first give as an example the detailed observations of one night, viz. February 25, 1911, at Mecca.

The given temperatures and barometer-readings are corrected ones. The level-readings given are each time the mean of the readings before and after those of the verniers, which nearly always agreed fairly well *inter se*. They represent the deviations of the position of the bubble from the middle of the graduation, whereby the sign is taken positive when the reading of the bubble was too low and the reading of the verniers had to be increased.

In the table the 1<sup>st</sup> and 2<sup>nd</sup> column contain the star and the position of the instrument; the 3<sup>rd</sup> column contains first the chronometer time of the pointing, then the hour angle derived from it; the 4<sup>th</sup> gives the readings of the two verniers, the 5<sup>th</sup> the employed zenithpoint. The remaining columns need no further explanation. Finally we have given the results for the latitude, such as follow from the observations of this night.



## DETERMINATION OF LATITUDE.

Mecca, 1911 February 25.

North star  $\alpha$  Aurigae Z  $24^{\circ}29'$ .South star  $\zeta$  Orionis 23 25.

		T. ext.	T. Bar.	Barom.	Level
$\alpha$ Aurigae	T. L.	28.3	28.9	735.1	+ 1.45 + 1.45
	T. R.	27.8	28.3	735.3	- 2.35 - 2.6
$\zeta$ Orionis	T. R.	27.8	28.3	735.3	+ 1.3 + 0.95
	T. L.	27.5	28.1	735.5	- 1.8 - 1.6

Star	Instr.	Chron. Time		Verniers	Zenithpoint	Refr.	Red. on merid.	Latitude
		Hour angle						
N.	T. L.	<sup>m</sup> 18	<sup>s</sup> 36 5	65°38' 20"	90° 9' 14".2	24".1	-1' 36".7	21°25'21".1
		- 5	37.0	245 38 30				
		22	14.0	65 45 30	15 18.3	24.0	- 12.0	4.9
	T. R.	-1	58.9	245 45 45				
		30	24.0	114 46 20	15 18.3	24.1	-1 58.2	27.9
		+ 6	12.6	294 46 40				
		34	33.0	114 43 50	9 14.2	24.1	-5 29.4	27.2
+10	22.3	294 44 10						
S.	T. R.	44	23.5	113 41 35	90 15 18.3	22.9	-2 40.8	21 25 3.4
		-5	55.1	293 42 5				
		48	11.0	113 33 20	9 14.2	22.9	- 20.6	9.4
	T. L.	- 2	7.0	293 33 50				
		56	16.5	66 42 25	9 14.2	22.9	-2 45.2	10.4
		+ 5	59.9	246 42 45				
		0	20.5	66 43 0	15 18.3	23.0	-7 45.4	32.9
+10	4.6	246 43 30						

Latitude North star  $21^{\circ}25'20''3$ 

,, South star 14. 0

,, Mean  $21^{\circ}25'17''2$

## RESULTS OF THE DETERMINATIONS OF LATITUDE AT JIDDA.

		North Star			South Star			North+South	
		T. L.	T. R.	Mean	T. L.	T. R.	Mean	$\frac{2}{2}$	
First Series									
1910		21°29'	21°29'	21°	21°29'	21°29'	21°	21°	
Nov.	18	Sch	16" 1	32" 9	29'24" 5	8" 3	12" 7	29'10" 5	29'17" 5
»	23	»		17.8	18.8	22.6	7.0	14.8	16.8
»	24	Sa	21.6	— 1.0	10.3				8.6
»	25	Sch	29.8	— 2.0	13.9	7.6	20.2	13.9	13.9
»	26	Sa	15.1	33.3	24.2	19.8	— 5.9	7.0	15.6
»	29	»	27.1	3.0	15.0	8.4	30.0	19.2	17.1
»	30	Sch	5.4	7.2	6.3	21.7	17.3	19.5	12.9
Dec.	1	Sa	21.1	— 0.5	10.3	—1.1	27.6	13.2	11.8
Second Series									
1911		Sa	21°29'	21°29'	21°	21°29'	21°29'	21°	21°
Jan.	25	»	15" 8	29" 8	29'22" 8	30" 0	3" 6	29'16" 8	29'19" 8
»	26	»	33.6	—5.4	14.1				12.4
»	28	»	2.7	38.3	20.5				18.8
»	30	»	27.8	9.3	18.6	7.3	34.3	20.8	19.7
»	31	»	29.9	16.9	23.4	5.2	16.0	10.6	17.0
Febr.	1	»	31.6	12.6	22.1	5.0	18.6	11.8	17.0
»	3	»	25.7	12.1	18.9	20.1	33.4	26.8	22.8
»	6	»	21.7	22.6	22.2	15.3	13.4	14.4	18.3
»	7	»	20.0	29.6	24.8	24.2	4.6	14.4	19.6
»	8	»	35.5	20.3	27.9	5.3	20.8	13.0	20.4
»	20	»	30.8	22.0	26.4	35.2	12.4	23.8	25.1
»	21	»	11.6		10.6	— 1.1	14.9	6.9	8.8
March	23	»	16.8	22.7	19.8	26.4	7.0	16.7	18.2



N. SCHELTEMA. "Determination of the geographical latitude and longitude of Mecca and Jidda executed in 1910-'11".  
Plate I.



Secondly there follow the results from all latitude determinations first from those at Jidda, subsequently from those at Mecca. In these tables have been collected the results from "Telescope left" and "Telescope right" for the north star and for the south star; the values given are the mean results of the pointings on the two threads.

On Dec. 1 and Febr. 21 no zenithpoint had been determined. For Dec. 1 we have used  $9^{\circ}9'4''$  and  $14^{\circ}43'5''$  and for Febr. 21 the mean of the results of Febr. 20 and 22. For Nov. 23 too a mean has been employed of that date itself and of Nov. 25, 28 and 30. On Nov. 23 and on Febr. 21 one star had not been observed in the two positions of the telescope.

For the few days on which the observations were not complete, we have in order to deduce mean results employed the systematic differences found hereafter. (See the table on p. 538).

RESULTS OF THE DETERMINATIONS OF LATITUDE AT MECCA.

		North Star			South Star			North+South 2
		T. L.	T. R.	Mean	T. L.	T. R.	Mean	
1911		$21^{\circ}25'$	$21^{\circ}25'$	$21^{\circ}$	$21^{\circ}25'$	$21^{\circ}25'$	$21^{\circ}$	$21^{\circ}$
Febr. 15	Sa	$21''5$	$11''5$	$25'16''5$	$3'9$	$30''1$	$25'17''0$	$25'16''8$
» 16	»	25.9	25.1	25.5	12.6	34.1	23.4	24.4
» 25	»	13.0	27.6	20.3	21.6	6.4	14.0	17.2
» 26	»				27.8	15.1	21.4	23.1
» 27	»	26.0	24.4	25.2	20.0	10.4	15.2	20.2
March 11	»	22.4	53.4	37.9	36.8	27.2	32.0	35.0
» 12	»				27.8	13.5	20.6	22.3
» 14	»	21.5	8.3	14.9	22.9	47.3	35.1	25.0
» 15	»	22.9	16.7	19.8	14.4	37.8	26.1	23.0
» 16	»	23.5	28.7	26.1	21.2	19.6	20.4	23.2

(To be continued).

**Astronomy.** — “*Determination of the geographical latitude and longitude of Mecca and Jidda executed in 1910—11.*” By Mr. N. SCHELTEMA. Part II. (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of June 29, 1912).

4. *Determination of the geographical latitude of Jidda and Mecca.*  
(Continued).

About the results given in the two preceding tables it must still be noted that some of them in the first series at Jidda depend on one pointing only. These are: Nov. 23 North star T. R., Nov. 29 North star T. L. and T. R. and Nov. 26 and Dec. 1 South star T. L. and T. R.

In the first place we shall now see what may be deduced about the accuracy of our observations as regards chance errors, from a comparison of the individual results.

If the mean error of one pointing on a star be . . . .  $m$   
 „ „ „ of one pointing on the signal be . . . .  $M$   
 then we have

m. error of the zenithpoint for the mean of the two threads  $\frac{1}{2} M$

(m. error)<sup>2</sup> of a zenithdistance derived from two pointings

on the star in one position of the telescope . . .  $\frac{1}{2} m^2 + \frac{1}{4} M^2$ .

We may now consider the m. error of a latitude  $\varphi$  to be equal to that of the zenithdistance from which it has been deduced and thus we obtain:

$$(\text{m. e.})^2 \text{ of } \varphi \text{ from one posit.} = \text{I} = \frac{1}{2} m^2 + \frac{1}{4} M^2$$

$$\text{„ of } \frac{1}{2} (\varphi_L - \varphi_R) = \text{II} = \frac{1}{4} m^2 + \frac{1}{4} M^2$$

$$\text{„ of } \frac{1}{2} (\varphi_L + \varphi_R) = \text{III} = \frac{1}{4} m^2$$

$$\text{„ of } \frac{1}{2} (\varphi_N - \varphi_S) = \text{IV} = \frac{1}{8} m^2$$

$$\text{„ of } \frac{1}{2} (\varphi_N + \varphi_S) = \text{V} = \frac{1}{8} m^2$$

$$\text{from which : II} + \text{III} = \text{I}$$

$$\text{II} - \text{III} = \frac{1}{4} M^2.$$

We now deduce the values of I, II, and III by comparing the individual results with their mean, first of all for the observations at Jidda and Mecca separately, afterwards for all together. In order to deduce in the latter case the values of II (just as afterwards of IV) the general mean of the  $\varphi_L - \varphi_R$  (and later on of the  $\varphi_N - \varphi_S$ ) has been employed. The result was, however, practically the same when the two separate means were used. The first series of observations at Jidda has been left out of account throughout this investigation, as it was less homogeneous and besides contained Mr. SALIM'S first observations, when he had had little practice as yet.

<i>Jidda</i>	<i>Mecca</i>	<i>Together</i>
I $(\pm 10''.86)^2 = 117.96$	$(\pm 10''.91)^2 = 119.08$	$(\pm 10''.88)^2 = 118.44$
II $(\pm 9''.67)^2 = 93.59$	$(\pm 8''.33)^2 = 69.40$	$(\pm 8''.99)^2 = 80.74$
III $(\pm 5''.29)^2 = 27.99$	$(\pm 7''.05)^2 = 49.71$	$(\pm 6''.09)^2 = 37.13$

From this appears very satisfactorily that  $II + III = I$ , while we find in the three cases :

$$II-III (\pm 8''.10)^2 = 65.60 \quad (\pm 4''.44)^2 = 19.69 \quad (\pm 6''.60)^2 = 43.61.$$

We can now compare *inter se* the values of  $m$  and  $M$ . As the signals at Jidda and Mecca were of a different kind the two values of  $M$  must not a priori be accepted as equal. The differences found between the  $m$  and  $M$  for the two places are, however, evidently not real, and we may only conclude from the general results that  $m$  and  $M$  are about equal, only possibly  $M$  slightly greater than  $m$ , which would also a priori be probable.

This investigation raises the question whether it would have been better to employ for the zenithpoint mean values from longer periods instead of the individual results, and although the value of the zenithpoint is generally eliminated, I still wanted to examine this. Therefore the observations have also been reduced with the zenithpoint from the whole of the period in which the instrument remained at one station, and then the squares of the mean error I and II have again been determined. As the last 3 isolated nights of observation at Jidda have not been used here, the values of I and II were also deduced again after the first way of calculation.

Thus we found:

<i>Jidda</i>	<i>Mecca</i>	<i>Together</i>
With individual zenithpoints		
I $(\pm 11''.00)^2 = 121.02$	$(\pm 10''.91)^2 = 119.08$	$(\pm 10''.96)^2 = 120.06$
II $(\pm 10''.02)^2 = 100.45$	$(\pm 8''.33)^2 = 69.40$	$(\pm 9''.22)^2 = 84.93$
With mean zenithpoints		
I $(\pm 9''.99)^2 = 99.88$	$(\pm 11''.68)^2 = 136.54$	$(\pm 10''.87)^2 = 118.21$
II $(\pm 8''.91)^2 = 79.31$	$(\pm 9''.32)^2 = 86.95$	$(\pm 9''.12)^2 = 83.13$

So no improvement is found for all the observations together; and although this is indeed the case for those at Jidda, the value of II remains still considerably higher than the one found for III, which shows that even when mean values are used the mean error of the zenithpoint has not yet become really small.

We shall now consider the values of IV and V, which, not taking into account the influences of flexure and division-errors, must be equal to  $\frac{1}{8}m^2$ . Now these two errors must have been almost eliminated in the  $\frac{1}{2}(\varphi_N + \varphi_S)$  owing to the nearly equal zenithdistance of North- and Southstar, but they may be considerable in the  $\frac{1}{2}(\varphi_N - \varphi_S)$ , and as on different nights couples of different zenithdistance were observed, the value of IV must also have been increased by that influence.

We now find, adding for comparison the values of  $\frac{1}{2} \cdot \text{III}$

	<i>Jidda</i>	<i>Mecca</i>	<i>Together</i>
IV	$(\pm 3''.36)^2 = 11.26$	$(\pm 4''.85)^2 = 23.51$	$(\pm 4''.14)^2 = 17.15$
V	$(\pm 4''.14)^2 = 17.12$	$(\pm 5''.06)^2 = 25.60$	$(\pm 4''.56)^2 = 20.76$
$\frac{1}{2} \cdot \text{III}$	$(\pm 3''.74)^2 = 14.00$	$(\pm 4''.99)^2 = 24.86$	$(\pm 4''.31)^2 = 18.56$

So we see that the values found for IV are not only not higher but on the contrary somewhat lower than those of V and that both are almost equal to  $\frac{1}{2} \cdot \text{III}$ , on which flexure and division-errors must have had some influence too. From this we may conclude that the two influences cannot have been great.

Coming now to a consideration of the mean results for  $\varphi$  in the different positions, we shall first compare those with the telescope left and right.

Denominating the correction of the employed zenithpoint  $\Delta Z$  then we see that

$$\begin{array}{lll}
 \text{Northstar } T. L. & \Delta \varphi = - \Delta Z & \\
 & T. R. & \Delta \varphi = + \Delta Z \quad \varphi_L - \varphi_R = + 2 \Delta Z \\
 \text{Southstar } T. L. & \Delta \varphi = + \Delta Z & \\
 & T. R. & \Delta \varphi = - \Delta Z \quad \varphi_L - \varphi_R = - 2 \Delta Z \\
 \text{Thus } . . . . . & & (\varphi_L - \varphi_R)_{\frac{1}{2}(N-S)} = + 2 \Delta Z
 \end{array}$$



In this way we find

$$\begin{aligned} \text{from all observations} \quad \Delta Z &= + 1''.5 \pm 1''.2 \\ \text{from those of 1911 only} \quad &+ 1''.0 \pm 1''.4 \end{aligned}$$

The value of  $\Delta Z$  is fairly small and almost equal to its mean error. The 3 partial results Jidda 1910, Jidda 1911 and Mecca have, however, the same sign. In order to correct one-sided observations we have employed the value deduced from 1911, Jidda and Mecca together,  $+ 1''.0$ .

In the second place we shall consider the differences between the results from the North and the Southstar. Except on one night in 1910 the zenith-distances of the observed stars lie between  $10^\circ$  and  $45^\circ$  and the mean  $z$  is about  $30^\circ$ . The  $\varphi_N - \varphi_S$  therefore contain twice the flexure for a zenith-distance of about  $30^\circ$  and the influence of the systematic division-errors on an arc of about  $60^\circ$ .

We now find:

$$\begin{aligned} \text{Jidda 1910 } \varphi_N - \varphi_S &= + 1''.7 \text{ weight } 5.5 \\ \text{,, 1911 ,,} &+ 5''.6 \text{ ,, } 11 \\ \text{Mecca ,,} &+ 0''.4 \text{ ,, } 8 \end{aligned}$$

from which follows for

$$\begin{aligned} \text{all observations together} &+ 3''.0 \pm 1''.7 \\ \text{for the observations in 1911} &+ 3''.4 \pm 1''.9 \end{aligned}$$

So the differences are not great. That the flexure of the telescope would be small was to be expected, but our results prove also that the systematic division-errors of the circle cannot be great. For the reduction of the incomplete observations we always employed (even in 1910), according to the results for 1911

$$\frac{1}{2} (\varphi_N - \varphi_S) = + 1''.7$$

In this manner we deduced for all observation-nights values for  $\frac{1}{2} (\varphi_N + \varphi_S)$ , and the means taken from these, giving half weight to the nights on which only one star had been observed, were considered our final results. Moreover mean values have been formed from the results in the separate positions and from the separate stars, again giving half weight to incomplete observations.

So we found:

	<i>Northstar</i>			<i>Southstar</i>			$\frac{Nth + Sth}{2}$
	<i>T.L.</i>	<i>T.R.</i>	Mean	<i>T.L.</i>	<i>T.R.</i>	Mean	
	Jidda						$21^\circ$
$1^\circ S.$	17".7	11".5	15".1	13".0	16".3	14".7	29' 14".5
$2^\circ S.$	23.3	19.2	20.9	15.7	16.3	16.0	29 18.5

	Mecca					21°
22"1	24"5	23"3	20"9	24"2	22"5	25' 23"1

The results from the two series for Jidda are :

$$21^{\circ} 29' 14''.5 \pm 1''.7$$

$$29 18 .5 \pm 1 .3$$

The difference between them a little exceeds the sum of their mean errors. Forming for the first series separate results for the two observers we obtain :

SCHELTEMA	21° 29' 15"1
SALIM	13.9

which are in good accordance.

After full consideration the two series have been united according to their weights and so our final results are :

$$q \text{ JIDDA } \quad 21^{\circ} 29' 17''.0 \pm 1''.0$$

$$q \text{ MECCA } \quad 21^{\circ} 25' 23''.1 \pm 1''.5$$

#### 5. *Results of the determinations of time.*

The determinations of time were always made by observing the altitude of a star in the east and of one in the west. Each star was observed in the two positions of the instrument and each time the transits over both the horizontal threads were noted, the instrument remaining clamped. Hence the zenithpoint for the mean of the two threads was employed in deducing the zenith-distance, and for the mean of the two instants the hour angle was then computed after the usual formula

$$\cos t = \frac{\cos z - \sin q \sin \delta}{\cos q \cos \delta}$$

In Nov.—Dec. 1910 the chronometer of Cummins and since the 2<sup>nd</sup> half of January 1911 that of Dent was used for the observations. The rates of Cummins were very great and irregular until it stopped altogether. I therefore omit the communication of the chronometer-corrections and rates for the first period. They were only used for the reduction of the latitude determinations and they were sufficiently accurate for that purpose.

About the determinations of time in the second period I shall first give the necessary data to form a judgment of the accuracy reached as regards systematic and accidental errors. The two following tables contain for this purpose the 4 separate results obtained each night.

As appears from these tables there is only one determination of time at Mecca (Febr. 26) which is not based on an eastern and

a western star, while on another night (Febr. 25) 2 eastern and 2 western stars were observed. Further, on Febr. 14 (Mecca) and Febr. 21 (Jidda) no zenithpoint was determined and this was derived from preceding and following days.

## RESULTS FROM THE DETERMINATIONS OF TIME AT JIDDA.

	Star East			Star West			E.—W.
	T. L.	T. R.	Mean	T. L.	T. R.	Mean	
1911			+ 2 <sup>h</sup>			+ 2 <sup>h</sup>	
Jan. 25	7 <sup>s</sup> 37	9 <sup>s</sup> 89	23 <sup>m</sup> 8 <sup>s</sup> 63	8 <sup>s</sup> 85	8 <sup>s</sup> 30	23 <sup>m</sup> 8 <sup>s</sup> 58	+ 0 <sup>s</sup> 05
" 26	15.77	14.46	15.11	13.86	13.12	13.48	+ 1.63
" 28	24.64	23.56	24.10	25.57	23.91	24.74	— 0.64
" 30	33.36	34.11	33.73	31.42	33.93	32.67	+ 1.06
" 31	38.61	37.24	37.93	36.00	38.05	37.02	+ 0.91
Febr. 1	41.61	40.44	41.02	40.34	41.05	40.70	+ 0.32
" 3	48.04	47.88	47.96	47.41	47.78	47.59	+ 0.37
" 6	0.47	59.27	59.87	59.72	0.14	59.93	— 0.06
" 7	5.08	4.57	24 4.82	5.08	4.80	24 4.94	— 0.12
" 8	10.03	8.16	9.10	7.96	9.15	8.56	+ 0.54
" 12	28.23	27.89	28.06	28.51	29.36	28.94	— 0.88
" 18	2.59	3.06	25 2.83	3.84	2.67	25 3.25	— 0.42
" 20	14.12	14.84	14.48	14.19	15.81	15.00	— 0.52
" 21	20.23	18.35	19.29	18.53	20.72	19.62	— 0.33
" 22	26.11	25.42	25.77	25.14	25.63	25.39	+ 0.38
Mrch 2	10.84	10.14	26 10.50	9.21	9.80	26 9.51	+ 0.99
" 3	13.89	14.17	14.03	14.70	13.83	14.26	— 0.23
" 7	30.96	30.37	30.67	30.23	29.85	30.04	+ 0.63
" 8	36.39	34.11	35.25	34.94	35.47	35.20	+ 0.05
" 19	27.96	27.28	27 27.62	26.29	29.18	27 27.74	— 0.12
" 20	32.53	33.26	32.89	34.41	32.78	33.60	— 0.71
" 21	37.60	37.72	37.66	37.55	38.17	37.86	— 0.20
" 23	47.84	48.75	48.30	48.32	47.84	48.08	+ 0.22

## RESULTS FROM THE DETERMINATIONS OF TIME AT MECCA.

	Star East			Star West			E.—W.
	T. L.	T. R.	Mean	T. L.	T. R.	Mean	
1911			+ 2 <sup>h</sup>			+ 2 <sup>h</sup>	
Febr. 14	20 <sup>s</sup> 13	15 <sup>s</sup> 53	27 <sup>m</sup> 17 <sup>s</sup> 83	16 <sup>s</sup> 06	19 <sup>s</sup> 38	27 <sup>m</sup> 17 <sup>s</sup> 72	+ 0 <sup>s</sup> 11
„ 15	24.72	22.43	23.57	22.04	23.87	22.96	+ 0.61
„ 16	28.24	26.49	27.37	28.73	28.86	28.80	— 1.43
„ 24	11.89	13.10	28 12.49	12.32	11.26	28 11.79	+ 0.70
„ 25	17.40	17.40	17.40	18.30	17.10	17.70	— 0.30
	17.69	18.34	18.02	18.55	18.09	18.32	— 0.30
„ 26				21.33	22.88	22.10	
„ 27	28.61	29.46	29.04	28.85	27.86	28.35	+ 0.69
Mrch 11	22.53	24.28	29 23.41	24.60	23.63	29 24.11	— 0.70
„ 12	27.27	28.05	27.66	27.00	26.99	27.00	+ 0.66
„ 14	38.92	38.22	38.57	38.71	38.44	38.57	0.00
„ 15	43.49	42.58	43.04	42.41	42.30	42.36	+ 0.68
„ 16	45.88	46.47	46.18	47.51	45.42	46.46	— 0.28
„ 17	50.40	50.29	50.34	50.32	49.17	49.75	+ 0.59

We must now first compare the results obtained in the two positions of the instrument. If the observed corrections of the chronometer are  $\Delta t$ , and the correction of the employed zenithpoint is designated by  $\Delta Z$ , then we find :

$$\text{Eastern star } \Delta Z = + a \frac{\Delta t_L - \Delta t_R}{2}$$

$$\text{Western star } \Delta Z = - a \frac{\Delta t_L - \Delta t_R}{2}$$

in which, if  $\Delta t$  is expressed in seconds of time and  $\Delta Z$  in seconds of arc, the mean value of the factor  $a$  is 13.8.

Leaving out of account the two days on which the zenithpoint had not been determined and reversing the signs for the western stars, we find as mean result :

$$\frac{\Delta t_L - \Delta t_R}{2} = + 0^s.07$$

from which follows  $\Delta Z = + 1''.0$ , i.e. the same value as was found from the determinations of latitude

Secondly the results from the eastern and the western star have been compared *inter se* and the mean values obtained were:

Jidda	23	nights	E—W = + 0 <sup>s</sup> .13
Mecca	13	,,	+ 0 .08
Together	36	,,	E—W = + 0 <sup>s</sup> .11

If this difference is produced by a constant error in the measured zenithdistances, then we find for its amount  $\Delta z = + 0''.8$ , while  $+ 1''.7$  had been found from the determinations of latitude in which the average zenithdistance was somewhat smaller. From a comparison of the separate values for E.—W. with their general mean we find, however, as mean error of the difference found in a single night  $\pm 0<sup>s</sup>.63$ , hence of the result from 36 nights  $\pm 0<sup>s</sup>.10$ , which is equal to the mean difference itself. The obtained results are, however, satisfactory, as we may conclude that no great unknown sources of error have been at work.

Disregarding a possible systematic personal error, we may further consider the mean error of  $\frac{1}{2}(E+W)$  as equal to that of  $\frac{1}{2}(E-W)$ , and we thus obtain as mean error of a chronometer-correction from an eastern and a western star  $\pm 0<sup>s</sup>.32$ .

At each time-determination the Leroy watches were compared with Dent. In the meantime Leroy 5180 = Dutch navy 3 had stopped and on the journeys to Mecca only 2 or 3 watches were taken (2 on the first and second journeys, 3 on the third) for fear of a possible mishap. Prudence demanded this, although now that everything went off well, I regret that all the watches were not taken each time. Naturally the mean errors of the observed corrections of the watches will be somewhat greater than in the case of Dent, owing to the errors of comparison.

The following tables contain the observed corrections for Dent and the Leroy-watches and the thence derived daily rates; the first two tables according to the observations at Jidda, the next two according to those at Mecca. On Febr. 25 Leroy 4129 = Dutch navy 77 was wound up too late after it had already stopped (see the tables on p. 548—550).

It is clearly visible from the daily rates contained in the preceding tables that the time-determination of Febr. 26 at Mecca, based on one star only, has been less accurate. The same appears with even greater force for the one of Febr. 21 at Jidda, although the observations of that night are apparently irreproachable.

For a closer investigation of the regularity of the watches we shall use the rates which have been obtained during the stay at

## CORRECTIONS DETERMINED AT JIDDA.

	DENT 2527			LEROY 5192 D. N. 7			LEROY 4129 D. N. 77	
	M.Time	Corr.	D. R.	M.Time	Corr.	D. R.	Corr.	D. R.
1911		+ 2 <sup>h</sup>			- 0 <sup>h</sup>		- 2 <sup>h</sup>	
Jan. 25	7 <sup>h</sup> 4 <sup>m</sup>	23 <sup>m</sup> 8 <sup>s</sup> 60		9 <sup>h</sup> 31 <sup>m</sup>	2 <sup>m</sup> 13 <sup>s</sup> 86		9 <sup>m</sup> 3 <sup>s</sup> 82	
" 26	7 49	14.30	+ 5 <sup>s</sup> 53	8 3	13.63	+ 0 <sup>s</sup> 24	1.85	+ 2 <sup>s</sup> 10
" 28	8 34	24.42	+ 4.98	7 58	8.70	+ 2.47	8 54.11	+ 3.88
" 30	7 17	33.20	+ 4.51	8 7	6.66	+ 1.02	47.25	+ 3.42
" 31	6 58	37.47	+ 4.33	9 10	4.78	+ 1.80	42.59	+ 4.46
Febr. 1	7 38	40.86	+ 3.30	9 39	2.22	+ 2.51	38.66	+ 3.85
" 3	7 20	47.77	+ 3.48	9 13	1 56.90	+ 2.68	30.50	+ 4.12
" 6	6 56	59.90	+ 4.07	9 29	49.45	+ 2.47	20.44	+ 3.34
" 7	7 56	24 4.88	+ 4.78	7 7	47.28	+ 2.41	16.08	+ 4.84
" 8	6 58	8.83	+ 4.11	10 6	45.49	+ 1.59	12.48	+ 3.20
" 12	8 16	28.50	+ 4.85	10 11	36.45	+ 2.26	7 58.24	+ 3.56
			+ 5.68			+ 1.87		+ 4.09
" 18	10 6	25 3.04	+ 5.92	10 48	25.21	+ 1.94	33.60	+ 4.83
" 20	9 30	14.74	+ 4.71	10 59	21.31	+ 0.74	23.91	+ 3.03
" 21	9 32	19.45	+ 6.61	10 9	20.60	+ 2.74	20.99	+ 5.41
" 22	7 48	25.58	+ 5.48	9 35	17.93	+ 1.13	15.71	
March 2	10 26	26 10.00	+ 4.25	11 22	8.84	- 0.54	51 20.24	+ 4.68
" 3	9 52	14.15	+ 4.12	10 22	9.36	+ 0.09	15.76	+ 4.52
" 7	8 20	30.36	+ 4.53	9 38	9.00	- 0.12	50 57.80	+ 4.35
" 8	10 6	35.23	+ 4.75	11 7	9.13	- 0.21	53.18	+ 5.12
" 19	11 1	27 27.68	+ 5.90	11 27	11.43	- 0.66	49 56.82	+ 5.64
" 20	9 38	33.24	+ 5.04	11 1	12.08	- 0.72	51.28	+ 4.83
" 21	7 8	37.76	+ 5.19	7 48	12.70		47.10	
" 23	7 23	48.19						

		LEROY 4127 D. N. 80		LEROY 3565 D. N. 81		LEROY 4128 D. N. 84		
		M. Time	Corr.	D. R.	Corr.	D. R.	Corr.	D. R.
1911			+ 2h		- 3h		- 2h	
Jan.	25	9h31m	18m34s56		26m44s61		57m42s23	
				+ 1s25		- 6s66		- 0s46
"	26	8 3	35.73	+ 2.49	50.86	- 5.83	42.66	+ 0.78
"	28	7 58	40.70	+ 1.97	27 2.50	- 5.60	41.10	- 0.27
"	30	8 7	44.65	+ 1.90	13.74	- 4.06	41.64	+ 0.44
"	31	9 10	46.63	+ 1.87	17.98	- 6.35	41.18	- 0.08
Febr.	1	9 39	48.54	+ 2.61	24.46	- 5.16	41.26	+ 0.19
"	3	9 13	53.71	+ 2.01	34.69	- 5.76	40.88	+ 0.28
"	6	9 29	59.76	+ 2.42	52.02	- 5.38	40.04	+ 0.42
"	7	7 7	19 1.94	+ 1.58	56.87	- 5.88	39.66	- 0.36
"	8	10 6	3.72	+ 1.81	28 3.48	- 5.39	40.07	+ 0.06
"	12	10 11	10.96	+ 0.47	25.04	- 5.02	39.83	- 0.09
"	18	10 48	13.80	+ 0.65	55.30	- 5.18	40.40	+ 0.25
"	20	10 59	15.10	- 0.72	29 5.70	- 6.69	39.89	- 1.54
"	21	10 9	14.41	+ 1.51	12.16	- 3.85	41.38	+ 1.10
"	22	9 35	15.88	+ 1.33	15.92	- 4.57	40.31	+ 0.08
March	2	11 22	26.58	+ 1.21	52.83	- 5.35	39.63	- 0.33
"	3	10 22	27.74	+ 1.68	57.96	- 5.19	39.95	- 0.06
"	7	9 38	34.41	+ 1.89	30 18.58	- 5.27	40.18	- 0.19
"	8	11 7	36.42	- 0.02	24.18	- 4.71	40.38	+ 0.47
"	19	11 27	36.18	+ 0.15	31 16.02	- 4.52	35.21	+ 0.35
"	20	11 1	36.33	- 0.48	20.46	- 4.64	34.87	+ 0.22
"	21	7 48	35.91		24.48		34.68	

## CORRECTIONS DETERMINED AT MECCA.

	DENT 2527			LEROY 5192 D. N. 7			LEROY 4129 D. N. 77	
	M. Time	Corr.	D. R.	M. Time	Corr.	D. R.	Corr.	D. R.
1911		+ 2h			+ 0h		- 2h	
Febr. 14	10h40m	27m17s78						
" 15	8 55	23.26	+ 5s91					
" 16	9 22	28.08	+ 4.73					
			+ 5.54					
" 24	8 32	28 12.14		12h47m	1m19s56		4m32s64	
			+ 5.70			+ 0s94	- 0h	
" 25	8 38	17.86	+ 4.30	8 16	20.32	+ 0.27	49 6.80	+ 3s15
" 26	8 16	22.10	+ 5.40	12 58	20.64	+ 1.67	3.03	+ 4.03
" 27	13 35	28.69	+ 4.68	14 6	22.39	+ 0.36	48 58.81	
Mrch 11	7 44	29 23.76	+ 3.53	8 17	26.65	+ 0.40		
" 12	8 0	27.33	+ 5.23	8 35	27.05	+ 0.15		
" 14	11 36	38.57	+ 4.01	13 0	27.38	- 2.45		
" 15	12 21	42.70	+ 3.63	13 28	24.88	- 1.39		
" 16	12 16	46.32	+ 4.62	13 15	23.50	+ 0.09		
" 17	7 39	50.05		8 18	23.57			

	LEROY 4127 D. N. 80			LEROY 3565 D. N. 81		LEROY 4128 D. N. 84	
	M. Time	Corr.	D. R.	Corr.	D. R.	Corr.	D. R.
1911		+ 2h			- 3h		- 2h
Febr. 14	11h 5m	21m47s67		25m58s53			
" 15	11 47	48.23	+ 0s54	26 4.27	- 5s58		
" 16	13 56	48.39	+ 0.15	11.91	- 7.01		
			+ 0.99				
March 11	8 17	22 10.87	- 0.02			55m 6s93	
" 12	8 35	10.85	+ 0.43			6.17	+ 0s75
" 14	13 0	11.79	+ 0.28			3.00	+ 1.45
" 15	13 28	12.08	- 0.38			1.71	+ 1.26
" 16	13 15	11.70	- 0.16			2.81	- 1.11
" 17	8 18	11.57				2.23	+ 0.73



Jidda. First we find as the mean daily rates during 4 periods of from 4 to 6 days each separated by journeys to Mecca:

	DENT	D.N. 7	D.N. 77	D.N. 80	D.N. 81	D.N. 84
Febr. 6—12	+ 4.72	+ 2.16	+ 3.68	+ 1.85	— 5.48	+ 0.03
„ 18—22	+ 5.77	+ 1.84	+ 4.53	+ 0.53	— 5.22	+ 0.02
March 2—8	+ 4.21	— 0.05	+ 4.51	+ 1.64	— 5.23	— 0.13
„ 19—23	+ 5.33	— 0.69	+ 5.26	— 0.15	— 4.58	+ 0.29

Secondly the accidental deviations have been examined, first by forming the mean value  $\frac{1}{n} \sqrt{\Sigma \Delta \Delta}$  of the differences  $\Delta$  between two subsequent daily rates, and afterwards by comparing the rates between Febr. 6 and March 23 themselves with their mean value for the whole period and deducing the mean deviation  $\frac{1}{n'} \sqrt{\Sigma' \Delta' \Delta'}$ .

Both these mean deviations I and II follow here.

	DENT	D.N. 7	D.N. 77	D.N. 80	D.N. 81	D.N. 84
I	$\pm 0.61$	$\pm 0.91$	$\pm 0.97$	$\pm 0.60$	$\pm 0.95$	$\pm 0.61$
II	$\pm 0.67$	$\pm 1.29$	$\pm 0.69$	$\pm 0.91$	$\pm 0.39$	$\pm 0.29$

For D.N. 81 the mean deviation I becomes  $\pm 0.57$ , if one time-determination is excluded.

The striking things in these comparisons are in particular the considerable acceleration of D.N. 7, owing to which also the mean deviation II is very great; and secondly the regularity of D.N. 84.

## 6. *Derivation of the difference of longitude Jidda—Mecca.*

From the corrections and rates of our watches given in the preceding paragraph we must now deduce the most probable value for the difference of longitude between Jidda and Mecca. Apart from the desirability of knowing the result yielded by each of the watches an immediate combination of the results of all would be impossible, because of the fact that on the different journeys different watches were taken and only Dent 2527 was used throughout. We shall therefore derive separately the results to which the 6 employed watches have led, and only afterwards we shall endeavour to derive from the whole of this material the most reliable final result.

Whereas each group of observations at Jidda or at Mecca usually includes time-determinations on 4 nights, determinations on 11 nights at Jidda, viz. from Jan. 25 to Febr. 12 immediately precede the

first journey to Mecca. But of however much value this long series is for the investigation of the watches and of the observations themselves, it cannot be of any immediate use for the derivation of the longitude. The longer the periods that are discussed the greater does the uncertainty become in the calculated rates and corrections of the watches, and soon its influence surpasses that of the errors of the observation. The great difficulty lying here in the answer to the question at what distance from the journey determinations of time may still be used to advantage, this will certainly not be the case for the observations in January. Finally only the observations of Febr. 6--12 have been used as a first group.

In the following we shall indicate Leroy's watches with the numbers they have in the Dutch Navy.

a. *Chronometer* DENT 2527.

This was taken by Mr. SALIM on all his journeys to Mecca and we have therefore at our disposal 4 groups of observations at Jidda, each including 4 nights, and between these 3 groups at Mecca with resp. 3, 3 and 6 determinations of time. Hence the discussion of the results obtained with this chronometer offers the best opportunity for comparing the different methods that may be followed for the deduction of the difference of longitude.

This deduction must be based on the comparison of observed chronometer-corrections at one place with interpolated corrections with regard to the local time of the other, whether that interpolation is made directly or in such a way, that we represent the corrections found for both stations by formulae differing only in the value of the constant term

An exhaustive criticism of these methods of calculation has been given by W. STRUVE on the occasion of his discussion of the results of the chronometer-expeditions <sup>1)</sup> executed between Pulkowa and Altona. He arrived at the conclusion that for observations made during a long period with a great number of journeys in both directions, as in his case, the representation by one formula, which must then contain a rather great number of powers of the time, would be unpractical. Our case, however, is somewhat different. The number of journeys and the duration of each was much less, and, whereas our determinations of time were much less accurate, we had attempted to make up for this inferiority by observing on several nights each time at each station.

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<sup>1)</sup> F. G. W. STRUVE. *Expéditions chronométriques entre Poulkova et Altona*. St.-Petersbourg 1844, p. 117—128.

It therefore was difficult for us to decide whether the different journeys would have to be discussed each by itself, or whether it would be preferable to take two or three together. And so finally it seemed best to follow both ways or rather try a number of different methods of calculation.

As the smallest group of observations discussed together we have always taken those obtained during the stay at one station combined with those from the preceding and the following visit to the other station. Then only a real interpolation is possible, and there is besides another circumstance demanding this. The rate of a chronometer may not only be subject to chance perturbations during the transport, but there may also take place a systematic retardation or acceleration, which continues throughout the duration of the transport. So a chronometer-correction calculated by means of extrapolation would be subject to systematic errors. On the other hand it is easy to see that in the calculation of a chronometer-correction for instance during a stay at Mecca from preceding and following observations at Jidda, the above mentioned error will be altogether eliminated for a moment exactly between those of the observations and that it would be small for other moments.

In this respect therefore such a group of observations can yield accurate results. A uniform retardation or acceleration, however, cannot be taken account of in this way but very imperfectly. This will become clear when we represent the chronometer-corrections by formulae. These will then contain terms with the square of the time, and it will be easily seen that in a combination Jidda—Mecca—Jidda the influence of such a term and that of an error in the difference of longitude will not differ greatly. If, however, a combination Mecca—Jidda—Mecca is also discussed then the influence of a quadratic term on the difference of longitude will have the reverse sign. Hence it will be possible to eliminate that influence by forming combinations of the two kinds and taking the mean of their results. This approaches already the calculation of a quadratic formula from a longer period.

I shall now communicate the numerical results obtained by means of Dent 2527 using the different methods of calculation.

### 1. *Results from the separate journeys.*

*Journeys to Mecca (J.—M.—J.).* Determinations of time in Mecca compared with interpolated values between the observations at Jidda immediately before and after the journey.

1 <sup>st</sup> journey		2 <sup>nd</sup> journey		3 <sup>rd</sup> journey	
+ 2 <sup>m</sup>		+ 2 <sup>m</sup>		+ 2 <sup>m</sup>	
Febr. 14	37 <sup>s</sup> 35	Febr. 24	35 <sup>s</sup> 44	Mrch 11	34 <sup>s</sup> 75
„ 15	37.57	„ 25	35.65	„ 12	33.52
„ 16	36.60	„ 26	34.49	„ 14	34.55
Mean	37 <sup>s</sup> 17	„ 27	34.39	„ 15	33.77
		Mean	34 <sup>s</sup> 99	„ 16	32.66
				„ 17	32.55
				Mean	33 <sup>s</sup> 63

Mean of the 3 journeys + 2<sup>m</sup> 35<sup>s</sup>26.

*Journeys to Jidda (Me—J—Me).* Treated in exactly the same way they gave the following results.

1 <sup>st</sup> journey		2 <sup>nd</sup> journey	
+ 2 <sup>m</sup>		+ 2 <sup>m</sup>	
Febr. 18	36 <sup>s</sup> 29	March 2	32 <sup>s</sup> 12
„ 20	35.53	„ 3	32.53
„ 21	36.37	„ 7	34.75
„ 22	35.38	„ 8	34.90
Mean	35 <sup>s</sup> 89	Mean	33 <sup>s</sup> 57

Mean of the 2 journeys + 2<sup>m</sup> 34<sup>s</sup>73.

The combinations Jidda—Mecca—Jidda have also been calculated by means of linear formulae, i.e. the corrections of the chronometer determined at Jidda and at Mecca have been represented resp. by formulae  $a + b(t-t_0)$  and  $a' + b(t-t_0)$ , from which the unknown quantities were solved after the method of least squares. The difference  $a' - a$  gives us the difference of longitude, or when a provisory value for this difference had been applied, the correction needed by that value. Of the 3<sup>rd</sup> group of observations at Jidda March 2 and 3 have only been used for the 2<sup>nd</sup> journey to Mecca, March 7 and 8 only for the 3<sup>rd</sup>.

So we found:

1 <sup>st</sup> journey	+ 2 <sup>m</sup> 35 <sup>s</sup> 62	(± 1 <sup>s</sup> 17)
2 <sup>nd</sup> „	35.62	(± 0.65)
3 <sup>rd</sup> „	32.93	(± 0.91)
Mean	+ 2 <sup>m</sup> 34 <sup>s</sup> 72	

The values in brackets are the mean residual errors in the observed chronometer-corrections, when they are represented by the calculated formulae.

## 2. Results from the whole of the material.

We have represented the observations by formulae of the second

and third degree

$$\frac{a}{a'} + b(t-t_0) + c(t-t_0)^2$$

and

$$\frac{a}{a'} + b(t-t_0) + c(t-t_0)^2 + d(t-t_0)^3$$

from which the values of the unknown quantities have been deduced by the method of least squares.

Five solutions have been found.

I by means of quadratic formulae

II by means of formulae of the 3<sup>rd</sup> degree .

III by means of quadratic formulae, correcting the data beforehand for the *supplementary* "transport-rate".

IV Like I, but giving half weight to the 6 observations of the 3<sup>rd</sup> series at Mecca.

V Like III, but giving half weight to the 6 observations of the 3<sup>rd</sup> series at Mecca.

Defining the supplementary "transport rate" E. as the excess of the daily rate during transport on that of the stationary chronometer and putting  $\tau$  for the duration of a transport, we have as supplementary correction of the chronometer after each journey

$$\Delta \text{ corr.} - \Delta_{stat} \text{ corr.} = \text{suppl. corr.} = \tau. E.$$

Now  $\Delta$  corr. could be determined from the time-determination next preceding and next following the transport, and yet be found, for the mean of two journeys to and fro, independent of an assumed value of the difference of longitude, while  $\Delta_{stat}$  corr. could be derived from the daily rates in the intervals next preceding and next following the transport.

In this way we found for the suppl. corr. after each transport:

1 <sup>st</sup> journey to M. and back	+ 2 <sup>s</sup> 22
2 <sup>nd</sup> " " " " "	+ 1.54
3 <sup>rd</sup> " " " " "	+ 1.60
	+ 1 <sup>s</sup> 79

Mean influence of one single journey + 1<sup>s</sup>79

i. e. the transport caused a retardation. This value was employed to correct the data for solutions III and V.

The solutions IV and V were executed not to give undue weight to the 3<sup>rd</sup> stay at Mecca with 6 observation-nights, overagainst the 1<sup>st</sup> and 2<sup>nd</sup> with 3 and 4 nights, since for each stay there are clearly left systematic errors. Febr. 26 was left out in all solutions. The 5 solutions gave for the difference of longitude.

I	+ 2 <sup>m</sup> 33 <sup>s</sup> 73	(± 1.84)
II	33.80	(± 1.85)
III	33.92	(± 1.58)
IV	34.23	(± 1.73)
V	34.38	(± 1.47)

The mean errors in brackets have the same meaning as above; in solutions IV and V they refer to observations with weight unity. Of all these solutions the 5<sup>th</sup> seems to me certainly to be preferable. I have, however, communicated also the other results, since they show the influence of the different ways of treating the observations. On the other hand I shall not give the results of a discussion of 2 successive journeys to Mecca together. The thus obtained formulae do not represent the observations better than the formulae deduced from the 3 journeys together.

The final result for Dent 2527 I should like to deduce as follows:

The 3 journeys J.—M.—J.	1 <sup>st</sup> meth.	+ 2 <sup>m</sup> 35 <sup>s</sup> 26
	2 <sup>nd</sup> meth.	34.72
	Mean	+ 2 <sup>m</sup> 34 <sup>s</sup> 99
The 2 journeys M.—J.—M.		+ 2 34.73
	Mean	+ 2 <sup>m</sup> 34 <sup>s</sup> 86
General solution		+ 2 34.38
Adopted final result		+ 2 <sup>m</sup> 34 <sup>s</sup> 62

(To be continued).

**Astronomy.** — “*Determination of the geographical latitude and longitude of Mecca and Jidda executed in 1910—11.*” By MR. N. SCHELTEMA. Part III. (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN.)

(Communicated in the meeting of September 28, 1912).

#### 6. *Derivation of the difference of longitude Jidda-Mecca.*

(Continued).

##### *b. Watch N<sup>o</sup>. 7.*

Watch N<sup>o</sup>. 7 was taken on the 2<sup>nd</sup> and 3<sup>rd</sup> journeys to Mecca. During the whole period of the observations it clearly showed a progressive acceleration. Any direct influence of the transport, however, was not clearly visible; nor was this so much to be feared for our carefully transported pocket-chronometers as for the box-chronometer of Dent.

From the observations with this watch results for the difference of longitude have again been derived in different ways.

1. *From the separate journeys.*

a. *Journeys Ji.—Me.—Ji.*; Jidda-time interpolated between the last time-determination before and the first after the journey.

2 <sup>nd</sup> journey		3 <sup>rd</sup> journey	
	+ 2 <sup>m</sup>		+ 2 <sup>m</sup>
Febr. 24	35 <sup>s</sup> 08	March 11	36 <sup>s</sup> 39
„ 25	34.92	„ 12	37.00
„ 26	33.89	„ 14	37.79
„ 27	34.46	„ 15	35.50
Mean	+ 2 <sup>m</sup> 34 <sup>s</sup> 59	„ 16	34.33
Omitting Febr. 26	34.82	„ 17	34.56
		Mean	+ 2 <sup>m</sup> 35 <sup>s</sup> 93

b. *Journey Me—Ji—Me*; discussed in the same manner.

March 2	+ 2 <sup>m</sup>	32 <sup>s</sup> 27
„ 3		33.13
„ 7		34.20
„ 8		34.72
Mean	+ 2 <sup>m</sup>	33 <sup>s</sup> 58

c. *Journeys Ji—Me—Ji*; all observations (including Febr. 26) represented by linear formulae

2 <sup>nd</sup> journey	+ 2 <sup>m</sup>	35 <sup>s</sup> 22	(± 2 <sup>s</sup> 48)
3 <sup>rd</sup> „		36.46	(± 1.05)

As the formulae for the second journey to Mecca represent the observations unsatisfactorily, I adopt as the result of this journey that of the direct interpolation excluding Febr. 26; for the 3<sup>rd</sup> I adopt the mean of the results *a* and *c*, hence:

2 <sup>nd</sup> journey	+ 2 <sup>m</sup>	34 <sup>s</sup> 82
3 <sup>rd</sup> „		36.20
Mean	+ 2 <sup>m</sup>	35 <sup>s</sup> 51

Combining this result with equal weights with result *b* we obtain  
+ 2<sup>m</sup> 34<sup>s</sup> 54.

2. *From general solutions by means of quadratic formulae.*

Of such solutions based on the whole material four have been executed; I and II respectively excluding and including Febr. 26; III and IV as I and II but giving half weight to the six observations during the 3<sup>rd</sup> stay at Mecca, for the same reason as in the case of Dent.

In this manner we found

I	+ 2 <sup>m</sup> 34 <sup>s</sup> 64	(± 0.90)
II	34.59	(± 0.88)
III	34.77	(± 0.80)
IV	34.70	(± 0.78)

I adopted the mean of the results III and IV, viz. + 2<sup>m</sup>34<sup>s</sup>74 and then as final result for watch N<sup>o</sup>. 7 the mean of the results from (1<sup>o</sup>) the individual journeys and (2<sup>o</sup>) the whole material together

$$+ 2^m 34^s 64$$

*c. Watch N<sup>o</sup>. 77.*

This watch was taken on the 2<sup>nd</sup> journey to Mecca, but unfortunately it stopped between the observations of Febr. 24 and 25, as it had been forgotten to be wound. For a comparison of the corrections determined at Mecca with corrections to Jidda-time we can therefore only use extrapolated values .

So we found :

Febr. 24	+ 2 <sup>m</sup> 33.41
„ 25	36.77
„ 26	35.10
„ 27	34.57
Mean I	+ 2 <sup>m</sup> 34 <sup>s</sup> 96
„ II	34.56
„ III	34.51

The first mean value was obtained by giving equal weights to the 4 days; for the 2<sup>nd</sup> we adopted weights inversely proportional to the interval of time, for which extrapolation had taken place; for the formation of the 3<sup>rd</sup> we moreover gave half weight to Febr. 26.

After all it seemed best to ignore the smaller weight of the last-mentioned time-determination, but to take into account the intervals of extrapolation and I therefore adopt as final result :

$$+ 2^m 34^s 56$$

*d. Watch N<sup>o</sup>. 80.*

This watch was taken to Mecca on the 1<sup>st</sup> and 3<sup>rd</sup> journeys. It did not seem advisable to immediately connect these two, which are separated by an interval of nearly one month. There is the same objection against forming the combination Me—Ji—Me. Hence we can only discuss two journeys Ji—Me—Ji each by itself, but then we meet with the difficulty that with linear interpolation the results are not free from the influence of a progressive variation in the daily



rate of the watch. If e.g. a daily *acceleration* of  $0^s.10$  takes place, then a linear interpolation in the middle between two time-determinations with an interval of 12 days will yield a result that is  $1^s.8$  in error and from a journey Ji--Me—Ji the difference of longitude will be found *so much too great*.

Now it appears, however, that the change of rate of N°. 80 was more complicated. When it was transported after a period of rest, it showed a considerable acceleration and then it continued for some time to show this accelerated rate unaltered. In such a case the error committed by linear interpolation will be much smaller, but it will not be easy to account for. Finally I have deduced results by means of quadratic formulae as well as by linear interpolation.

We thus found :

*1<sup>st</sup> Journey.*

*a.* By interpolation between the last preceding and the next following observations at Jidda

Febr. 14	+	2 <sup>m</sup> 35 <sup>s</sup> 75	
15		35.83	
16		35.48	
Mean	+	2 <sup>m</sup> 35 <sup>s</sup> 69	
<i>b.</i> By linear formulae	+	2 <sup>m</sup> 37 <sup>s</sup> 85	(± 1 <sup>s</sup> 63)
<i>c.</i> By quadratic formulae	+	2 <sup>m</sup> 35 <sup>s</sup> 05	(± 0 <sup>s</sup> 72)

As the linear formulae represent the observations very unsatisfactorily, the result thus obtained was rejected and we adopted as the result yielded by the 1<sup>st</sup> journey the mean of the results *a* and *c*

$$+ 2^m 35^s.37.$$

*3<sup>rd</sup> Journey.*

*a.* By interpolation between the nearest observations at Jidda

March 11	+	2 <sup>m</sup> 34 <sup>s</sup> 51	
12		34.51	
14		35.49	
15		35.80	
16		35.44	
17		35.33	
Mean	+	2 <sup>m</sup> 35 <sup>s</sup> 18	
<i>b.</i> By linear formulae	+	2 <sup>m</sup> 35 <sup>s</sup> 69	(± 0 <sup>s</sup> 59)
<i>c.</i> By quadratic formulae	+	2 <sup>m</sup> 33 <sup>s</sup> 92	(± 0 <sup>s</sup> 49)

For the solutions  $b$  and  $c$  only March 7 and 8 were used as first Jidda-group, as the next preceding observations are 4 days earlier.

I adopted the mean of the 3 results  $a$ ,  $b$  and  $c$

$$+ 2^m 34^s 93$$

As the final result yielded by N°. 80 I adopt the mean of the results from the two journeys

$$+ 2^m 35^s 15$$

*e. Watch N°. 81.*

This watch was taken on the first journey to Mecca. About that time it seems to have gone fairly regularly,

The following results were found for the difference of longitude.

First we obtain by means of comparison of the results obtained at Mecca with those interpolated between the last preceding and the next following observations at Jidda :

Febr. 14	+	2 <sup>m</sup> 36 <sup>s</sup> 74
15		- 36.17
16		33.99
Mean	+	2 <sup>m</sup> 35 <sup>s</sup> 63

Further 4 general solutions have been executed, I and III by quadratic, II and IV by linear formulae. Only for III and IV the deviating result of Febr. 21 at Jidda was excluded.

I	+	2 <sup>m</sup> 35 <sup>s</sup> 81	(± 0 <sup>s</sup> 88)
II		35.39	(± 0.85)
III		35.78	(± 0.83)
IV		35.22	(± 0.83)

It appears here, as before, that the exclusion of a deviating time-determination between others has but little influence. As results from the quadratic and from the linear formulae I adopt the mean of I and III and that of II and IV

$$+ 2^m 35^s 80$$

and

$$+ 2 35.30$$

and as final result the mean of the results obtained by the three methods, direct interpolation, linear and quadratic formulae

$$+ 2^m 35^s 58$$

*f. Watch N°. 84.*

This was taken on the 3<sup>rd</sup> journey. According to the investigation of the results at Jidda its rate was very regular; it showed no progressive variation and only small accidental deviations. During the stay at

Mecca, however, it had a daily rate, in the mean  $+ 0^s.78$ , which differed much from that at Jidda and was moreover very irregular, while during the journeys themselves the rate seems to have had about the same value as at Jidda.

The following results were derived from this watch:

1<sup>st</sup> by interpolation between the nearest determinations of time at Jidda.

March 11	$+ 2^m 32^s10$
„ 12	32.38
„ 14	34.52
„ 15	35.33
„ 16	33.77
„ 17	33.98
Mean	$+ 2^m 33^s68$

2<sup>nd</sup> by means of quadratic formulae. Using also the observations of March 2 and 3, which are further away from the time of the journey, or leaving them out, we obtained

$$\begin{array}{r} + 2^m 34^s72 \\ \text{or} \quad \quad \quad 32.83 \end{array} \quad \begin{array}{l} (\pm 1^s03) \\ (\pm 1.08) \end{array}$$

3<sup>rd</sup> We obtained in the same two manners by means of linear formulae:

$$\begin{array}{r} + 2^m 33^s08 \\ \text{or} \quad \quad \quad 33.64 \end{array} \quad \begin{array}{l} (\pm 1^s27) \\ (\pm 1.02) \end{array}$$

Of the results by the quadratic formulae the mean of the two has been adopted; of those by the linear formulae it seemed best to adopt the second.

Giving finally equal weight to the results of the 3 methods, the final result becomes;

$$+ 2^m 33^s70$$

differing rather much from those yielded by the other watches.

*g. General result from the 6 watches.*

For the derivation of the difference of longitude according to each of the employed watches, given in the preceding paragraphs, different methods of calculation were followed, which had all of them special advantages and disadvantages, and in most cases the mean of the results found by these different methods was adopted. Naturally in this procedure some arbitrariness could not be avoided; its influence on our final results, however, will not be great.

Now there remains to be decided what weight must be given to each of the 6 results. Although it seemed at first that for each watch we should have to adopt a different accuracy peculiar to it, it appeared after all very difficult to determine this intrinsic accuracy. So e.g. for N<sup>o</sup>. 84 we should have had to adopt a rather high weight according to the observations at Jidda and yet it went very irregularly during the journey to Mecca. So ultimately I adopted the same intrinsic accuracy for each of the watches; nor could greater weight be given to the chronometer of Dent, *as a travelling instrument*, than to Leroy's watches.

Hence I have given weights to the 6 results proportional to the number of journeys in which each watch had been used, and besides only a weight of 0.5 to watch 77 owing to the discontinuity during the stay at Mecca.

So I obtained:

DIFFERENCE OF LONGITUDE JIDDA—MECCA.

DENT	2527	+	2 <sup>m</sup> 34 <sup>s</sup> 62	Weight	3
WATCH	7		34.64	„	2
„	77		34.56	„	0.5
„	80		35.15	„	2
„	81		35.58	„	1
„	84		33.70	„	1

From the agreement of these six values *inter se* there follows as mean error for weight unity  $\pm 0^s.66$  and the final result from the 6 watches is found to be

**Difference of longitude + 2<sup>m</sup> 34<sup>s</sup>74  $\pm$  0<sup>s</sup>22.**

It is clear from the foregoing that a derivation of the difference of longitude from partial results for each journey must lead to a less advantageous combination of the observations. Yet I want to show that a final result obtained in this way does not differ much from the above given.

We then obtain, indicating the journeys Ji.—Me.—Ji. and Me.—Ji.—Me. respectively by M. and J.

	M I	M II	M III	J I	J II
DENT	36 <sup>s</sup> 40	35 <sup>s</sup> 30	33 <sup>s</sup> 28	35 <sup>s</sup> 89	33 <sup>s</sup> 57
7		34.82	36.20		33.58
77		34.56( $\frac{1}{2}$ )			
80	35.37		34.93		
81	35.58				
84			33.70		
<b>Mean</b>	35 <sup>s</sup> 78	34 <sup>s</sup> 96	34 <sup>s</sup> 53	35 <sup>s</sup> 89	33 <sup>s</sup> 58

Combining these 5 results with equal weights we should find

$$+ 2^m 34^s.95$$

which agrees with the final result adopted by us just within the limit of its mean error.

7. *Reduction of the results to known points in the two cities.*  
*Longitude of Mecca from the meridian of Greenwich.*

The situation of the observation-station at Jidda, (the Dutch consulate) relative to the Mecca-gate has been measured four times by Mr. SALIM by means of the determination of the direction and the length of the 4 parts of the road, the first by the boussole, the last by counting the steps, the length of which was found to be equal to  $0^m.768$ . To the directions counted from magnetic North to East first of all must be added, to reduce them into astronomical azimuths, the magnetic declination for which, according to the English admiralty chart,  $-2^\circ.4$  was adopted. The thus corrected results, however, appear to be still in need of a correction of  $+1^\circ.6^1$ ) according to the results obtained with the same instrument about the road from Jidda to Mecca, of which we shall treat hereafter. So the total correction of the lectures of the boussole was  $-0^\circ.8$ .

From the directions and distances the rectangular co-ordinates have been derived taking as axes the parallel and the meridian. The mean results of the 4 measurements expressed in meters were as follows (see Plate II, fig. I, the scale of which has been given in hectometers):

	$\Delta x$	$\Delta y$
$b-a$	— 94 <sup>m</sup>	+ 350 <sup>m</sup>
$c-b$	— 313	+ 92
$d-c$	0	— 14
$e-d$	— 58	— 27
Sum	— 465 <sup>m</sup>	+ 401 <sup>m</sup>

The sums of the two first  $\Delta x$  and  $\Delta y$  give as co-ordinates of the Medina-gate relative to the Mecca-gate  $-407^m$  and  $+442^m$ , for which is found  $-368^m$  and  $+349^m$  according to the English admiralty-chart *Jidda with its approaches*. I adopted the mean of the two results and thus found as co-ordinates of the Dutch consulate relative to the Mecca-gate:

<sup>1)</sup> The accurate result is  $+2^\circ.0$ , but this difference is here immaterial.

$$\Delta x = -446^m \quad \Delta y = +355^m \text{ } ^1)$$

or expressed in seconds of longitude and latitude :

$$\Delta \lambda = 15''.5 \text{ West} \quad \Delta \varphi = 11''.5 \text{ North.}$$

For the determination of the relative situation of the observation-station Mecca and the Ka'bah we have a report of Mr. SALIM that the latter is at 187 steps S.S.W. of the former. After this indication it has been tried to identify the observation-spot in the plan of Mecca by BURCKHARDT, as revised by SNOUCK HURGRONJE, of which the scale has been given in steps. As the most likely place we have found the spot indicated on Plate II, Fig. 2, as point III, which is situated at a distance of 192 steps from the Ka'bah, indicated as point I, in a direction  $13^\circ$  East of the North.

The rectangular co-ordinates of the observation-station relative to the Ka'bah thus are :

$$\begin{array}{ll} \Delta x = +35^m & \Delta y = +144^m \\ \text{or} \quad \Delta \lambda = 1''.2 \text{ East} & \Delta \varphi = 4''.7 \text{ North} \end{array}$$

As regards the mean errors of the values for  $\Delta \lambda$  and  $\Delta \varphi$ , I believe that they are not undervalued if we adopt  $\pm 2''.5$  for both co-ordinates for Jidda and  $\pm 1''.5$  for Mecca.

So we obtain :

$$\text{Latitude Jidda Mecca-gate} \quad 21^\circ 29' 5''5 \pm 2''7$$

$$\text{Latitude Mecca Ka' bah} \quad 21^\circ 25' 18''4 \pm 2''1$$

$$\text{Difference of longitude} \quad 38' 24''4 \pm 4''4 = 2^m 33^s 63 \pm 0.29$$

The thus obtained latitude may be compared with the result found in 1876 by Comm. WHARTON, on which the Adm. chart is based.

The point determined by him is situated on Geziret el Mifsaka and the latitude he found was  $+21^\circ 28' 0''$ . Further we find by measurement on the chart that the latitude of the Mecca-gate is  $2197^m = 1' 11''.4$  greater. Hence it becomes  $21^\circ 29' 11''.4$  i. e.  $6''$  greater than the value found by us, an agreement which, if we take into account the reductions that had to be added to both results before their comparison, may be considered satisfactory.

In the second place WHARTON's result for the longitude of Jidda may be employed to determine the longitude of Mecca from the meridian of Greenwich. He found as longitude of his observation-spot  $39^\circ 11' 25''$ ; according to the chart the Mecca-gate is situated

<sup>1)</sup> These results may be compared with the co-ordinates of the English consulate, which is next to the Dutch, measured on the admiralty-chart, as accurately as was possible: :  $\Delta x = -542^m \quad \Delta y = +344^m$ .

Our plate II, fig. 1 is based solely on Mr. SALIM's measurements.

2010<sup>m</sup> = 1'9"8 further eastward, hence:

Longitude Jidda. Mecca-gate  $39^{\circ}12'34''.8 = 2^{\text{h}} 36^{\text{m}} 50^{\text{s}}.32$

and consequently:

Longitude Mecca Ka'bah  $39^{\circ}50'59''.2 = 2^{\text{h}} 39^{\text{m}} 23^{\text{s}}.95$ .

We have still attempted to find out the basis of WHARTON'S longitude and whether the telegraphic determinations of the longitude of Aden and Suez have been employed for it. But although Rear-admiral C. J. DE JONG, Chief of the Dutch Dept. of Hydrography has with the greatest kindness put all the available charts and other data at our disposal, we have not succeeded in obtaining certainty.

Direct data as to the basis of WHARTON'S longitude were not to be found. Then we tried to attain our end by consulting the charts of Aden, Suez and Alexandria and by comparing the longitudes given there with the results of the telegraphic determinations. These had been executed principally in connection with the transit of Venus in 1874, and have been discussed by AIRY <sup>1)</sup>, COPELAND <sup>2)</sup> and AUWERS <sup>3)</sup>. We did not find any certainty in this way either, as in the first place it is not sure that the bases for the longitude in the different charts agree *inter se*, and moreover uncertainty as to the exact situation of the observation-spots prevented an accurate determination of the longitude errors of the charts.

Therefore it seemed impossible to find out with any probability the correction needed for the longitude of Jidda adopted in the Adm. Chart. Consequently I must regard the longitude of Mecca as deduced above, as the most reliable value for the present.

In order to find the total mean error of the longitude of Mecca from the meridian of Greenwich, we should have to know that of the adopted longitude of Jidda, and it is impossible even to estimate this. In the total mean error an unknown value  $m_J$  has therefore been included.

Thus our final results for the geographical position of Mecca Ka'bah become

**Latitude**  $+ 21^{\circ} 25' 18''.4 \pm 2''.1$

**Longitude**  $39^{\circ} 50' 59''.2 \pm \sqrt{(4''.4)^2 + m_J^2}$

OR  $2^{\text{h}} 39^{\text{m}} 23^{\text{s}}.95 \pm \sqrt{(0^{\text{s}}.29)^2 + m_J^2}$  **East of Greenw.**

<sup>1)</sup> G. B. AIRY: Account of observations of the transit of Venus, 1874, Dec. 8. London 1881.

<sup>2)</sup> Dun Echt observatory publications. Vol. III. Dun Echt 1885.

<sup>3)</sup> A. AUWERS: Die Venus-Durchgänge 1874 und 1882. Bd. 6. Berlin 1896.

The results obtained by J. HESS from the itinerary Jidda-Mecca were:<sup>1)</sup>

Latitude  $21^{\circ} 21'.7 \pm 3'.8$

Longitude  $39^{\circ} 52'.5 \pm 3'.2$

i. e. agreeing with our result within the given mean errors, which are still rather considerable. So we may conclude that by our work, the accuracy attained has been a great deal increased.

Finally we shall compare our results for Jidda and Mecca with those of ALI BEY. The following are the corrections needed by the latter

	$\Delta \varphi$	$\Delta \lambda$
Jidda	$- 3' 36''$	$+ 6' 35''$
Mecca	$- 2' 51''$	$- 24' 1''$

ALI BEY's errors in latitude are for both places about  $-3'$ ; the errors in longitude are great and irregular, which need not surprise us, as they are the results from observed lunar distances (for the longitude of Jidda also 2 observations of eclipses of Jupiter-satellites have been taken into account). ALI BEY also determined the latitude of a number of other places in Arabia. Perhaps these also need a correction of about  $-3'$  and may then be fairly reliable. I dare not, however, decide this question here.

### 8. Road from Jidda to Mecca.

In this last paragraph I shall discuss the results obtained by Mr. SALIM in surveying the road between the two places, on a journey on foot from Mecca to Jidda, undertaken for this special purpose. This survey was made by means of observations with the boussole and by counting the steps.

The boussole, of which mention has been made before, was a very handy little instrument by Casella, belonging to the Leyden observatory. It has a little telescope in which also the divisions of the azimuth-circle (full degrees) are made visible by reflexion.

The following table contains the results of these observations and their further reduction. The road was divided into 92 parts, for each of which the direction and the length were determined. For the two terminal and 13 of the 91 intermediate points special names could be indicated in the first column. The 2<sup>nd</sup> and 3<sup>d</sup> columns contain for each of the parts of the road the direction  $\alpha$  read on the boussole and the length  $l$  expressed in steps.

The directions  $\alpha$  are counted from magnetic North to East, South

<sup>1)</sup> HESS started from the following co-ordinates of Jidda, Mecca-gate: Longitude  $39^{\circ} 11' 47''$  E; Latitude  $+ 21^{\circ} 29' 11''$ , while the Adm. Chart Ed. 1905 gives  $39^{\circ} 12' 35''$ ;  $+ 21^{\circ} 29' 11''$ , i.e. a longitude of  $48''$  greater.



	$\alpha$	$l$	$x$ $\Sigma l' \sin \alpha'$	$y$ $\Sigma l' \cos \alpha'$	$x$ corrected	$y$ corrected
1 Entrance Mecca						
1—2	337°	496	— 166	+ 350	— 130	+ 299
2 Kahwat al-mu'allim						
2—3	245	606	— 586	+ 132	— 489	+ 128
3—4	291	760	— 1148	+ 321	— 956	+ 304
4—5	240	320	— 1359	+ 187	— 1138	+ 197
5—6	264	230	— 1536	+ 161	— 1287	+ 180
6—7	307	595	— 1918	+ 425	— 1601	+ 413
7—8	306	2090	— 3276	+ 1327	— 2716	+ 1212
8—9	288	1418	— 4341	+ 1624	— 3602	+ 1493
9—10	265	2100	— 5966	+ 1413	— 4976	+ 1363
10—11	275	484	— 6344	+ 1430	— 5292	+ 1388
11 Umm ed-dûd						
11—12	275	699	— 6888	+ 1454	— 5749	+ 1425
12—13	227	959	— 7413	+ 921	— 6206	+ 991
13—14	243	370	— 7664	+ 779	— 6421	+ 880
14—15	252	611	— 8110	+ 613	— 6801	+ 753
15—16	236	818	— 8623	+ 235	— 7244	+ 451
16—17	267	1284	— 9621	+ 141	— 8086	+ 401
17 Maktala						
17—18	267	1623	— 10881	+ 22	— 9148	+ 337
18—19	235	1278	— 11672	— 583	— 9832	— 148
19—20	249	2907	— 13754	— 1483	— 11608	— 844
20—21	246	1254	— 14631	— 1918	— 12359	— 1184
21 Kahwat Sâlim						
21—22	255	1400	— 15673	— 2245	— 13244	— 1427
22—23	289	2531	— 17565	— 1680	— 14819	— 898
23 'Alameyn						
23—24	298	4710	— 20878	— 93	— 17559	+ 534
24—25	314	1150	— 21549	+ 503	— 18105	+ 1055

	$z$	$l$	$\frac{x}{\Sigma l' \sin z'}$	$\frac{y}{\Sigma l' \cos z'}$	$x$ corrected	$y$ corrected
25 Shumésî						
25—26	315°	1427	— 22368	+ 1256	— 18772	+ 1712
26—27	319	1102	— 22958	+ 1881	— 19250	+ 2255
27—28	280	402	— 23268	+ 1922	— 19509	+ 2298
28—29	252	350	— 23524	+ 1827	— 19727	+ 2226
29—30	269	806	— 24151	+ 1790	— 20256	+ 2213
30—31	258	922	— 24848	+ 1611	— 20847	+ 2084
31—32	250	687	— 25343	+ 1407	— 21269	+ 1926
32—33	246	614	— 25772	+ 1194	— 21636	+ 1760
33—34	255	330	— 26018	+ 1117	— 21845	+ 1702
34—35	265	970	— 26768	+ 1019	— 22478	+ 1642
35 small kahwah						
35—36	250	567	— 27177	+ 851	— 22827	+ 1513
36—37	272	2189	— 28884	+ 839	— 24263	+ 1552
37 Hadda						
37—38	268	1202	— 29818	+ 766	— 25051	+ 1518
38—39	239	443	— 30107	+ 576	— 25299	+ 1367
39—40	250	845	— 30717	+ 325	— 25819	+ 1174
40—41	244	772	— 31247	+ 39	— 26274	+ 949
41—42	234	336	— 31452	— 124	— 26451	+ 818
42—43	250	906	— 32106	— 393	— 27009	+ 611
43—44	257	1994	— 33605	— 806	— 28281	+ 307
44—45	235	706	— 34043	— 1141	— 28659	+ 39
45—46	230	785	— 34495	— 1554	— 29052	— 296
46—47	225	1930	— 35514	— 2662	— 29941	— 1197
47—48	223	506	— 35771	— 2962	— 30166	— 1442
48—49	217	491	— 35989	— 3277	— 30358	— 1701
49—50	220	2782	— 37313	— 4995	— 31521	— 3106
50 Bahra						
50—51	240	277	— 37495	— 5110	— 31679	— 3198
51—52	225	318	— 37663	— 5293	— 31825	— 3347

	$z$	$l$	$x$ $\Sigma l' \sin z'$	$y$ $\Sigma l' \cos z'$	$x$ corrected	$y$ corrected
52—53	240°	250	— 37828	— 5398	— 31966	— 3430
53—54	238	755	— 38314	— 5731	— 32385	— 3696
54—55	250	1153	— 39146	— 6073	— 33095	— 3959
55—56	261	1205	— 40067	— 6259	— 33875	— 4088
56—57	280	4594	— 43618	— 5786	— 36847	— 3586
57—58	270	150	— 43735	— 5791	— 36946	— 3587
58—59	281	519	— 44135	— 5730	— 37280	— 3524
59 Kahwat al-'abd						
59—60	281	210	— 44297	— 5705	— 37415	— 3498
60—61	253	356	— 44559	— 5797	— 37638	— 3569
61—62	317	1056	— 45146	— 5219	— 38115	— 3065
62—63	312	583	— 45496	— 4930	— 38401	— 2811
63—64	297	502	— 45852	— 4767	— 38695	— 2664
64—65	305	2296	— 47360	— 3801	— 39935	— 1807
65—66	319	1392	— 48106	— 3012	— 40539	— 1123
66—67	295	776	— 48664	— 2780	— 41002	— 911
67—68	250	1743	— 49921	— 3298	— 42074	— 1309
68—69	267	780	— 50527	— 3355	— 42585	— 1340
69—70	295	1733	— 51775	— 2836	— 43619	— 867
70—71	292	610	— 52223	— 2677	— 43991	— 720
71 Kattâna						
71—72	306	438	— 52508	— 2488	— 44226	— 552
72—73	290	1575	— 53679	— 2117	— 45199	— 206
73—74	275	317	— 53926	— 2106	— 45407	— 190
74—75	295	453	— 54252	— 1970	— 45677	— 66
75—76	296	390	— 54530	— 1848	— 45907	+ 45
76—77	290	1490	— 55638	— 1497	— 46828	+ 372
77—78	310	1084	— 56308	— 981	— 47377	+ 826
78 Jarâda						
78—79	310	1930	— 57501	— 63	— 48353	+ 1633
79—80	280	416	— 57822	— 20	— 48622	+ 1678

	$z$	$l$	$x$ $=$ $\Sigma l \sin z'$	$y$ $=$ $\Sigma l \cos z'$	$x$ corrected	$y$ corrected
80—81	265°	1470	— 58959	— 167	— 49582	+ 1589
81—82	256	1225	— 59875	— 438	— 50360	+ 1388
82—83	280	3400	— 62503	— 88	— 52560	+ 1759
83 Raghâma						
83—84	288	7024	— 67779	+ 1385	— 56952	+ 3152
84—85	299	5866	— 71869	+ 3435	— 60332	+ 4995
85—86	290	1233	— 72785	+ 3725	— 61094	+ 5266
86—87	289	4440	— 76103	+ 4716	— 63855	+ 6197
87—88	284	460	— 76455	+ 4788	— 64149	+ 6268
88—89	287	366	— 76731	+ 4860	— 64378	+ 6337
89—90	293	780	— 77300	+ 5074	— 64850	+ 6533
90—91	281	424	— 77627	+ 5124	— 65124	+ 6585
91—92	285	583	— 78071	+ 5223	— 65495	+ 6681
92—93	283	330	— 78324	+ 5271	— 65705	+ 6729

93 Jidda, Mecca-gate

and West, from  $0^\circ$  to  $360^\circ$ . They had first to be reduced to astronomical azimuths counted also from North to East and for this purpose the magnetic declination was taken from the Adm. Chart of Jidda. For 1911 it was assumed to be  $2^\circ 55'$  West —  $11 \times 3' = 2^\circ.4$  West, and this value was considered to hold good for the whole of the road. As length of the step  $0^m.78$  was adopted as given by Mr. SALIM, and the length of the parts of the road expressed in meters shall be designated by  $l'$ . The 4<sup>th</sup> and 5<sup>th</sup> columns contain the co-ordinates  $x$  and  $y$  in meters of points 2—93 relative to point 1, taking as axes the parallel and the meridian, so that we have

$$x = \Sigma l' \sin \alpha' \quad y = \Sigma l' \cos \alpha'$$

in which for point  $n$  the summation has to be extended over all the parts between point 1 and  $n$ .

The two values in the last line of the 4<sup>th</sup> and 5<sup>th</sup> columns of the table are the co-ordinates of the Mecca-gate at Jidda relative to the Entrance of Mecca. These may be compared with the corresponding differences deduced from the astronomical determinations. For this

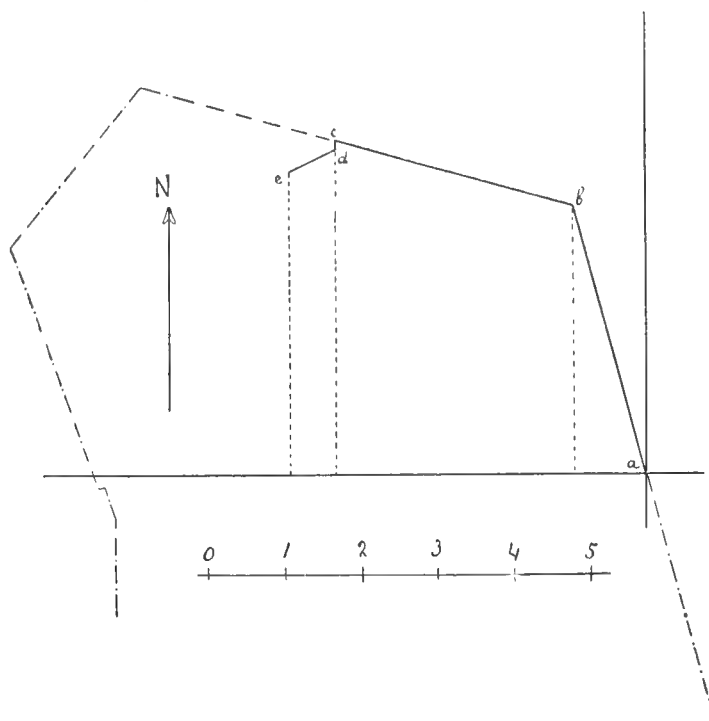


Fig. 1.

**Observation-station at Jidda.**

- a* Mecca-gate,
  - c* Medina-gate.
  - abc* Part of the rampart.
  - e* Observation-station, Dutch Consulate.
- Scale in hectom.

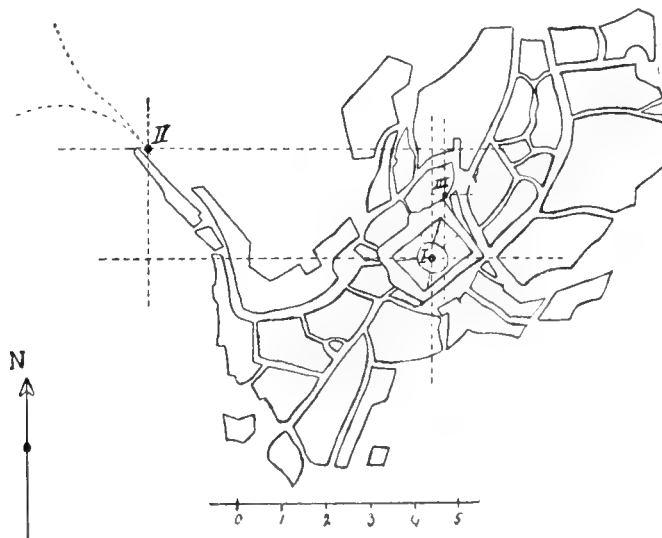


Fig. 2.

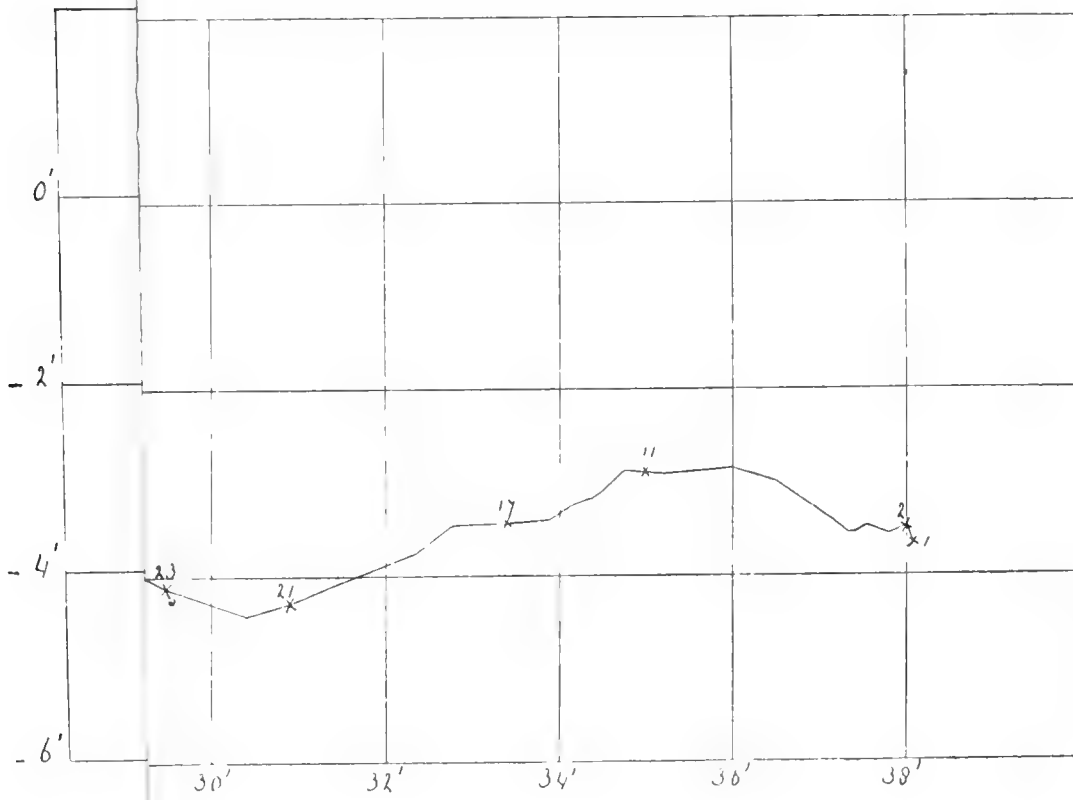
**Observation-station at Mecca.**

- I Ka'bah.
  - II Entrance to the town on the Jidda side.
  - III Observation-station.
- Scale in hectom.



N.

Plate III.



- 1 Mecca
- 2 Kahw
- 11 Umm

- 78 Jarâda.
- 83 Raghâma.
- 93 Jidda Mecca-gate.

Proceed



Road from Jidda to Mecca.

1 Mecca Entrance to the town  
2 Kahwat al mu allim.  
11 Umm ed dud.

17 Maktala  
21 Kahwat Salm  
23 Alamyra.

25 Shumesi  
35 small kahwah  
37 Haikda.

50 Bahra  
59 Kahwat al abd  
71 Kattana

78 Jarida  
83 Raghama  
93 Jidda Mecca-gate



purpose the situation of the point designated as "Entrance Mecca" had first to be determined. We adopted as such point II in the plan of Mecca, plate II fig. 2, and according to this its co-ordinates relative to the Ka'bah are

$$\Delta x = 638 \text{ m.} = 22''.2 \text{ West}$$

$$\Delta y = 253 \text{ m.} = 8''.2 \text{ North}$$

Using these values we obtain as relative co-ordinates of points 93 and 1 according to the astronomical determinations

$$X = -38' 2''.2 = -65705 \text{ m}$$

$$Y = +3' 38''.9 = +6729 \text{ m}$$

while the results from the observations on the journey were

$$x = -78324 \text{ m} \quad y = +5271 \text{ m.}$$

As the errors in the astronomical results may be regarded as small compared with the accumulated errors of the observations on the journey, we may conclude that the latter results need corrections  $\Delta x = +12619 \text{ m}$   $\Delta y = +1458 \text{ m}$ . We may regard these corrections as owing to an error in the accepted value for the length of a step and to a constant error in the deduced azimuths.

We then obtain, designating the true length of a step in meters by  $0.78(1-p)$  and the constant error of the azimuths by  $\sigma$ , the two equations

$$\Delta x = -(p \cos \sigma + 1 - \cos \sigma)x + (1-p)y \sin \sigma = +12619$$

$$\Delta y = -(p \cos \sigma + 1 - \cos \sigma)y - (1-p)x \sin \sigma = +1458$$

The solution of the two equations yields

$$p \cos \sigma + 1 - \cos \sigma = a = +0.15913$$

$$(1-p) \sin \sigma = b = +0.02932$$

So the true length of a step and the constant error of the azimuths are found to be

$$(1-p) 0^m.78 = 0^m.6563 \quad \sigma = +2^\circ 0'$$

while the values found for  $a$  and  $b$  may be used to correct the co-ordinates of our 92 points. These corrected co-ordinates are found in the two last columns of our table.

At the same time they have also been drawn, and with them the whole of the road Mecca—Jidda, in our plate III. No scale has been appended, but in the map itself lines have been drawn at distances of  $2'$  in longitude and latitude of each other. These have been drawn perpendicular to each other, and as length of a second of latitude and longitude in meters we have accepted after BESSEL'S dimensions of the earth  $30^m.753$  and  $28^m.789$ , the latter value holding rigorously for  $\varphi = 21^\circ 27'$ . As the absolute longitude from the meridian of

Greenwich may still need a correction, we have reckoned the longitude and also the latitude on the map from Jidda, Mecca-gate.

At the conclusion of this paper, which has proved that much advice and help has come to me from many sides, the only thing left for me to do, is to express my sincere gratefulness to all those from whom I have received this help.

*Postscript.*

(November 1912).

In order to investigate the accuracy of our time-determinations we had compared the results from the eastern and the western star, but in doing this no attention had been paid to the fact, that in most cases the times of observation of the two stars lie too far apart to neglect the rate of the chronometer in the interval.

Therefore this comparison has been made anew after correcting the differences E—W; the results, however, have not been materially changed. We now obtained

Jidda 23 nights	E—W =	+	0 <sup>s</sup> .12
Mecca 13	.,		+ 0 .23
Together	E—W =	+	0 <sup>s</sup> .16 ± 0 <sup>s</sup> .10

against before + 0<sup>s</sup>.11 ± 0<sup>s</sup>.10. The constant error in the zenith-distances would be found now  $\Delta z = + 1''.$ 2 against before + 0''<sup>.</sup>8, but just as before it is small.

As mean error of the difference from one night we now found ± 0<sup>s</sup>.58 and therefore as mean error of a time-determination from two stars ± 0<sup>s</sup>.29 against before ± 0<sup>s</sup>.32. The accordance of the two stars was somewhat improved.

**Chemistry.** — “*On a new modification of sulphur*”. By Dr. A. H. W. ATEN. (Communicated by Prof. HOLLEMAN).

Communicated in the Meeting of September 28, 1912.

This investigation originated in an observation by ARONSTEIN and MEIHWIZEN <sup>1)</sup>, who noticed that when a solution of sulphur in sulphur chloride (S<sub>2</sub>Cl<sub>2</sub>), supersaturated at the temperature of the room, is heated to 170°, no sulphur crystallises on cooling. I have afterwards repeated this experiment and demonstrated that the solution of S in S<sub>2</sub>Cl<sub>2</sub>, which has been heated to 170° not only fails to deposit sulphur at the temperature of the room, but is even capable of dissolving a

<sup>1)</sup> Verhandelingen Kon. Akad. Wet. Amsterdam, 1898. 1.

considerable quantity of sulphur, about as much as the solution saturated at 20° originally contained<sup>1)</sup>. It also appeared that the conversion, which has taken place here retrogrades very slowly, for after 20 days the quantity of dissolved sulphur had decreased but very little.

The sulphur which was added originally as rhombic sulphur and consequently was present in the liquid as  $S_\lambda$  apparently undergoes some conversion or other on heating, for after the heating some  $S_\lambda$  has disappeared. The question now arises: what has become of this  $S_\lambda$ ? Does it pass into another modification of sulphur or is there a compound formed of S with  $S_2Cl_2$ ? At one time I thought I ought to arrive at the latter conclusion, because in other solvents metaxylene for instance, the same phenomenon could not be observed. KRUYT<sup>2)</sup> on the other hand is of opinion that the cause of the disappearance of  $S_\lambda$  is situated in a transformation into amorphous sulphur  $S_\mu$ . From what follows it will appear that neither of these views is correct.

I have again resumed the investigation of the above phenomenon in consequence of a publication by ROTINJANZ<sup>3)</sup>, in which are communicated the results of the determinations of the viscosity of sulphur at different temperatures with and without addition of iodine.

With molten sulphur without iodine, the course of the viscosity, as function of the temperature to which the sulphur has been heated, may be readily explained, because a transformation  $S_\lambda \rightleftharpoons S_\mu$  takes place which proceeds comparatively slowly, so that with more rapid changes in temperature there exists no equilibrium between the two kinds of molecules. On rapid cooling, for instance the condition is such as corresponds with an equilibrium at a higher temperature. If, however, we endeavour to apply the same explanation to molten sulphur to which a trace of iodine has been added, we meet with difficulties as will be shown in a more elaborate article to appear shortly. The course of the viscosity cannot be explained here by the assumption that in the molten sulphur the above transformation  $S_\lambda \rightleftharpoons S_\mu$  takes place. Presumably, a third modification of sulphur occurs here, as an iodine-sulphur compound does not exist, at least not in the solid condition. The same may now happen with mixtures of sulphur and sulphur chloride.

The investigation was, therefore, directed in the first place to decide what becomes of the  $S_\lambda$  when this is heated with  $S_2Cl_2$  to a

1) Z. für physikalische Chemie. **54**. (1905). 88.

2) Z. für physikalische Chemie. **64**. (1908). 545.

3) Z. für physikalische Chemie. **62**. (1908). 609.

suitable temperature. As has already been observed it is possible that either a compound of S with  $S_2Cl_2$  is formed or else another sulphur modification. That, in this latter case, there can be no question of the formation of  $S_\mu$  is shown readily from the following experiments.

On heating S with  $S_2Cl_2$  we can obtain very concentrated sulphur solutions. If this were caused by the formation of  $S_\mu$ , this ought to have a great solubility, or the separation of  $S_\mu$  ought to take place very slowly when, by heating, a concentrated solution of  $S_\mu$  has been obtained. Neither of these phenomena occur, however. If sulphur which, owing to heating and rapid cooling, contains a certain quantity of  $S_\mu$  is brought into contact with  $S_2Cl_2$  a turbid liquid is formed immediately. This turbidity of  $S_\mu$  is permanent at the ordinary temperature, but on warming for a few minutes at  $100^\circ$ — $110^\circ$  it disappears. On cooling, however, the turbidity at once reappears. Hence, it is shown that the solution and subsequent separation of  $S_\mu$  is a process which takes place without appreciable retardation. At the temperature of the room, the solubility of  $S_\mu$  is very trifling, for the experiment just described may be carried out with a very little  $S_\mu$ . At a higher temperature the solubility is apparently fairly large. At  $100^\circ$ — $110^\circ$  an appreciable, rapid transformation of  $S_\mu$  takes place, presumably into  $S_\lambda$ , for if the above experiment is repeated a few times, the turbidity of  $S_\mu$ , finally, does not reappear.

Not only in pure  $S_2Cl_2$  but also in  $S_2Cl_2$  containing  $S_\lambda$  the solubility of  $S_\mu$  is but small, although the solubility of  $S_\mu$  in  $S_2Cl_2$  is increased by addition of  $S_\lambda$ . For, on adding to  $S_2Cl_2$  which is turbid by  $S_\mu$  a *large* quantity of  $S_\lambda$ , the turbidity disappears, but only when very *little*  $S_\mu$  has been added. The possibility of the formation of  $S_\mu$  in considerable quantities in solution is therefore excluded.

In order to ascertain what is formed from the  $S_\lambda$  originally present, the proper way would be to determine the melting point line of the system  $S + S_2Cl_2$  after heating. It appeared, however, that nothing else but rhombic sulphur or  $S_2Cl_2$  was separated. The newly formed product does not separate at all. As, moreover, no suitable chemical method could be found to separate the new product from the other, systematic determinations were carried out of the solubility of sulphur in mixtures that had been heated to a suitable temperature. From this it can also be shown whether a new modification or a compound has formed.

The system  $S + S_2Cl_2$  must be treated as a ternary system, as besides  $S_\lambda$  and  $S_2Cl_2$  a third kind of molecule is present. The composition of a mixture that has been heated for a certain time must,

therefore be represented in a triangle the apexes of which indicate :  $S_2$ ,  $S_2Cl_2$ , and the compound, or the new modification.

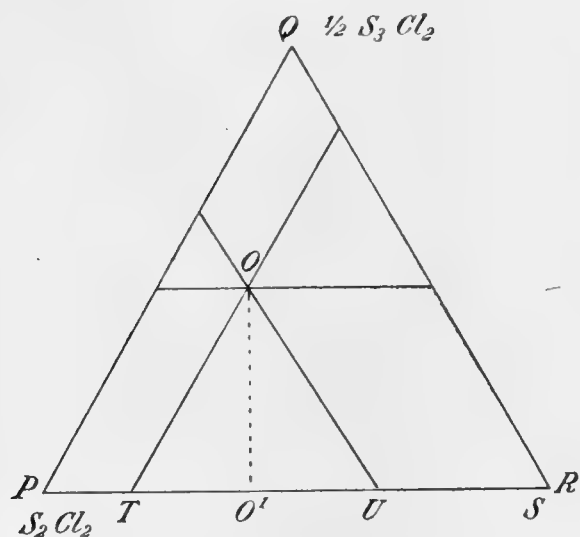


Fig. 1.

If  $O$  is the real composition, a mixture of this composition  $O$  contains  $PTSRU$   $S_2Cl_2$  and  $UT$   $\frac{1}{2} S_3Cl_2$ . The gross composition is now :

$$\frac{\text{total } S}{\text{total } S_2Cl_2} = \frac{PT + \frac{1}{2}UT}{RU + \frac{1}{2}UT} = \frac{PO'}{RO'}$$

Hence,  $O'$  gives the gross composition. This is also the composition which one may determine experimentally by an estimation of the total sulphur. Not, however, the true composition  $O$ , for there is no means of determining the quantity of  $S_3Cl_2$ .

The question now arises: If we heat the mixture of varying sulphur content to a given temperature and then cool to a definite temperature, how then does the composition of the solution saturated after warming, vary with the original composition? This is readily indicated with the aid of fig. 2.

Let the line  $PBHR$  represent the equilibrium  $S + S_2Cl_2 \rightleftharpoons S_3Cl_2$  at a temperature  $T_1$ .

Let  $TDFU$  represent the solubility line of  $S_2$  in mixtures of  $S_2Cl_2$  and  $S_3Cl_2$  at the temperature  $t_1$ . The point  $T$  then represents the solubility of  $S_2$  in  $S_2Cl_2$ .

When now a mixture of  $S$  and  $S_2Cl_2$  of the gross composition  $A$  is heated long enough at  $T_1$  the equilibrium  $S + S_2Cl_2 \rightleftharpoons S_3Cl_2$ , which belongs to the temperature  $T_1$ , sets in. The inner composition is, therefore, given by a point of the curve  $PBHR$ , which is found by drawing a line  $\perp PR$  in the gross composition of  $A$ . The intersecting point of this perpendicular line with  $PBHR$  gives the looked for real composition. If one now cools rapidly to  $t_1$  the composition  $B$

will not alter if the equilibrium at  $T_1$  remains the same. This liquid now must separate sulphur at  $t_1$ ; the saturated solution must lie on

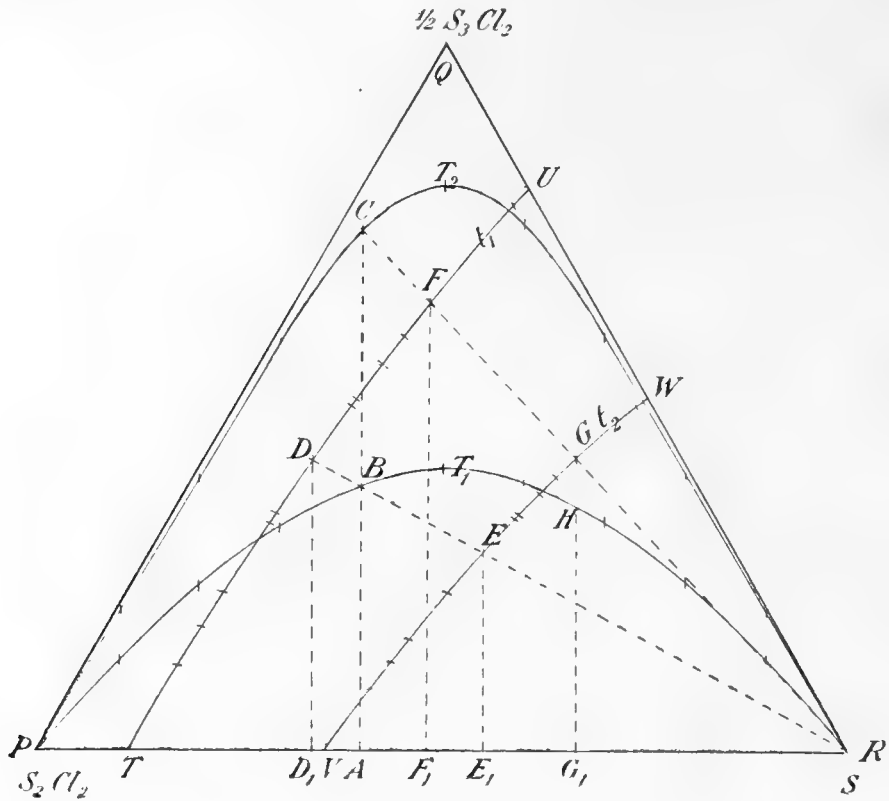


Fig. 2a.

the line  $TDFU$ . Its composition is found by drawing from  $R$  a straight line through  $B$  until this intersects the solubility line  $TDFU$ . In this manner we find for the real composition of the saturated solution  $D$ , the corresponding gross composition is  $D_1$ .

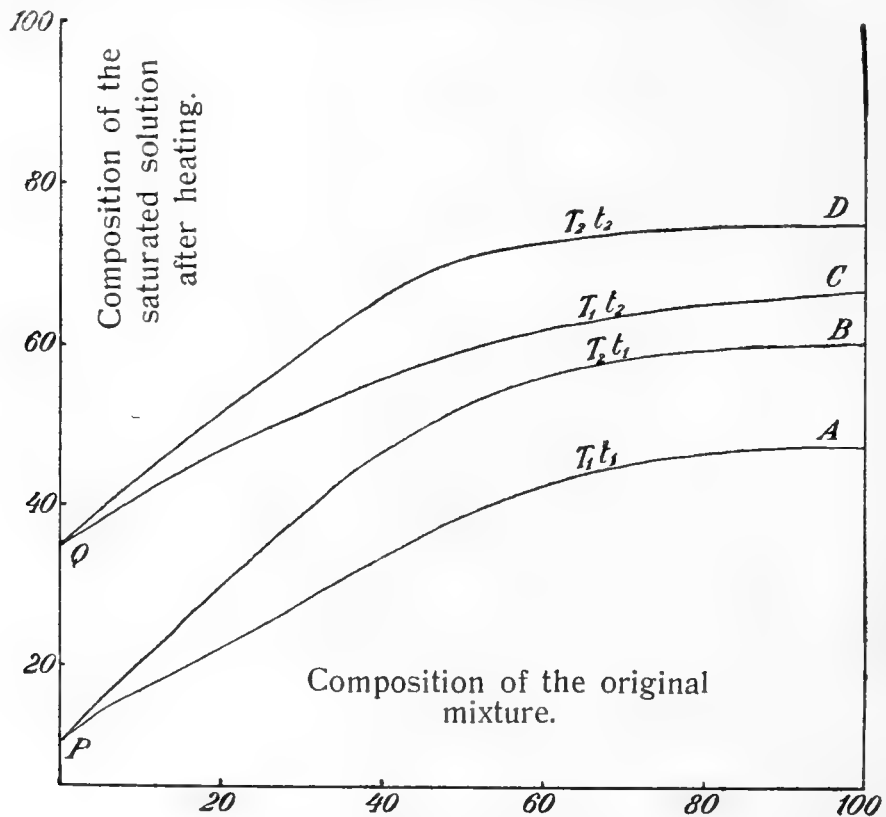


Fig. 2b

We can carry out this construction for different gross compositions and then put down the composition of the solutions saturated at  $t_1$  after heating at  $T_1$  as function of the original composition. We then find the line  $PA$  in Fig. 2*b*.

When we determine the solubility line at a higher temperature  $t_2$ , the line  $QC$  is found. If we heat at a higher temperature  $T_2$  and again determine the solubility at  $t_1$  and  $t_2$ , the lines  $PB$  and  $QD$  are found.

We see that these lines, at 100 at. % S of the original composition, approach to a certain limitation value which is different for different temperatures of heating and of solubility. This limitation value can give a larger as well as a smaller sulphur content than corresponds with the composition of the compound.

The first is the case when the compound is but little dissociated and the solubility of the sulphur is great, the latter when the dissociation is great and the solubility small.

Quite different becomes the course of these solubility lines when a new modification of sulphur is formed. In this case, the composition of a ternary system is given by a point in a triangle the apices of which indicate  $S_2Cl_2$ ,  $S$ , and the new sulphur modification. We then obtain the gross composition (for instance  $D_1$  in Fig. 3*a*)

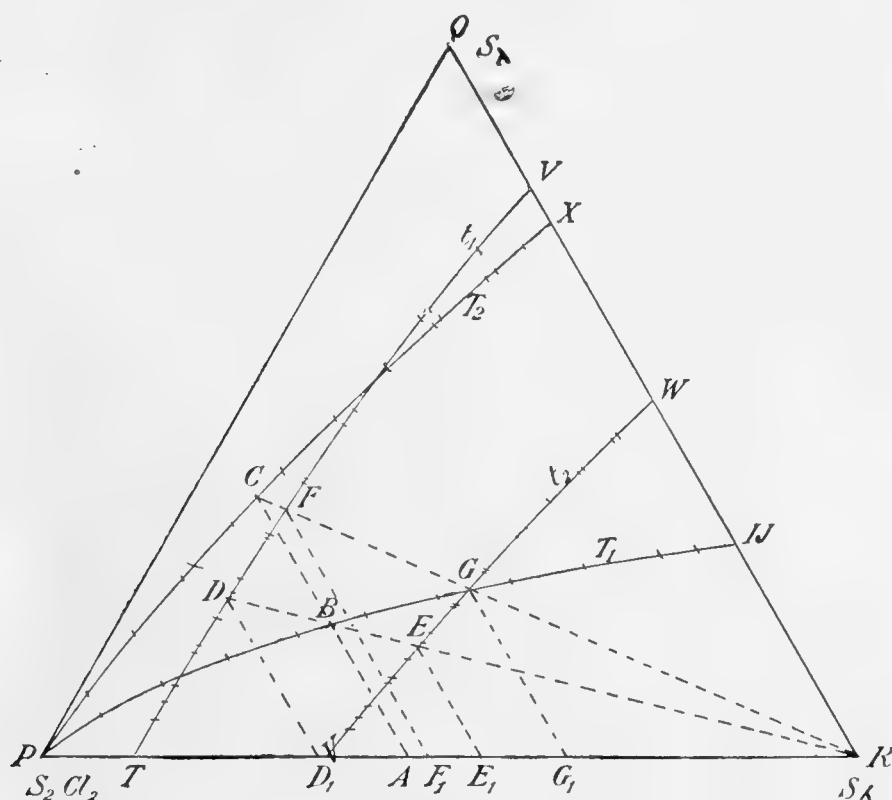


Fig. 3*a*.

by drawing a line  $// QR$  through  $D$  which indicates the real composition. The line indicating the inner equilibrium between  $S$  and

the new modification of sulphur will now have the course of  $PBGY$  in Fig. 3<sup>a</sup> for a temperature  $T_2$ . The solubility line of  $S_\lambda$  in mixtures of  $S_2Cl_2$  and the new modification will be  $TDFV$  at the temperature  $t_1$ .

We can now deduce in exactly the same manner as in Fig. 2<sup>a</sup>

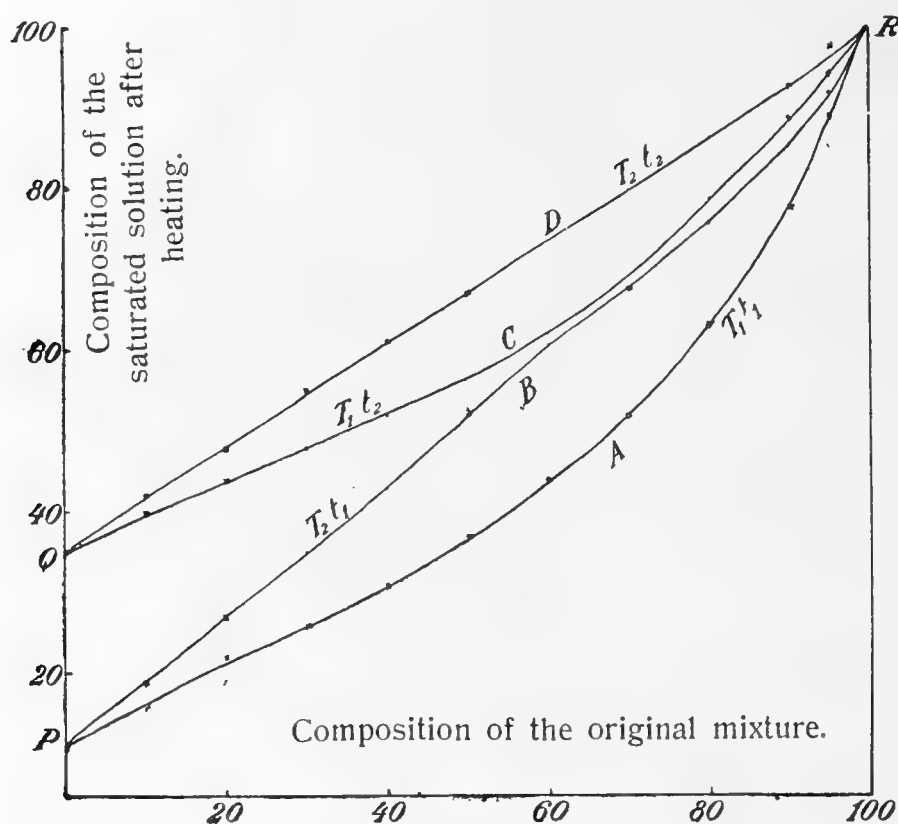


Fig. 3b.

what is the gross composition of a given mixture, which after heating to  $T$ , is saturated with  $S_\lambda$  at  $t_1$ . If we do this with different compositions we find that the composition of the saturated solution as a function of the original composition is given by the line  $PAR$  in Fig. 3<sup>b</sup>. If we repeat the same construction for mixtures which are heated to  $T_2$  and for solubilities at  $t_1$  and  $t_2$  we find the lines  $PBR$ ,  $QCR$  and  $QDR$ . These lines all converge in one point. At 100 at. %  $S$  of the original composition, the composition of the saturated solution is also 100 at. %  $S$  the temperature to which the mixture was heated or independently of temperature at which the solubility has been determined.

Hence, there exists a characteristic difference between the course of the solubility line with a compound and a new modification. Therefore, it was expected that in this manner we might decide with which of the two cases we are dealing here.

Before proceeding to the actual solubility determinations it was ascertained at what temperature the transformation of  $S_\lambda$  becomes



perceptible and how long the heating must be continued before the equilibrium is attained. It now appeared that a very perceptible conversion already occurs at 100°. Whereas, at 0° the solubility of S<sub>2</sub> in S<sub>2</sub>Cl<sub>2</sub> without previous heating amounts to 36.1 at. % of S, this, after heating to 100°, becomes 55.7 at. % of S for a 50 at. % mixture. The heating, therefore, causes a considerable increase in solubility. It also appeared that at 100° 1½ hour was required for the equilibrium to set in. This reaction, therefore, proceeds at 100° comparatively slowly and it may be expected that by rapid cooling the equilibrium can be fixed at 100°. Above 100° it is different. Because, as a rule, the velocity of a reaction for every 10° of rise in temperature becomes 2—3 times greater, the setting in of the equilibrium will, at 140°, require about 5 minutes and at 170° less than one minute. Here we shall not be able to cool so rapidly that the equilibrium becomes fixed and hence we shall find, after heating to 170°, somewhat fluctuating values for the solubility. This explains why the determinations previously carried out at 170° agreed badly. At a lower

TABLE I.

Original composition at % S	Composition of the saturated solution at		
	25° at % S	0° at % S	— 60° at % S
0	53.5	36.1	11.6
10.0	57.6	40.1	18.1
28.7	62.0	47.4	31.9
49.6	—	55.7	—
49.9	66.6	56.0	42.9
60.1	69.4	59.9	47.7
69.1	72.8	—	—
79.4	—	72.0	65.2
80.1	—	71.6	66.1
89.9	82.1	—	—
90.1	—	80.5	—
94.6	87.7	—	—
97.4	91.0	—	—
98.0	93.5	—	—

temperature than  $100^\circ$ , the completion of the equilibrium takes a longer time and it can be fixed with still greater certainty.

The method of investigation is very simple. A mixture of sulphur and sulphur chloride is heated for a sufficient time at the desired temperature. The liquid is then cooled rapidly, sulphur is added if the solution is not already saturated and the whole shaken at the temperature at which we want to know the solubility. When the solution is saturated a sample of the liquid is taken and its composition determined. This determination is carried out by oxidation with *aqua regia* and bromine, evaporation of the volatile acids and titration of the residual sulphuric acid.

In the first place, mixtures of varying composition were heated to  $100^\circ$  and the solubility determined at  $25^\circ$ ,  $0^\circ$  and  $-60^\circ$ .

The results are united in table I. (see p. 579).

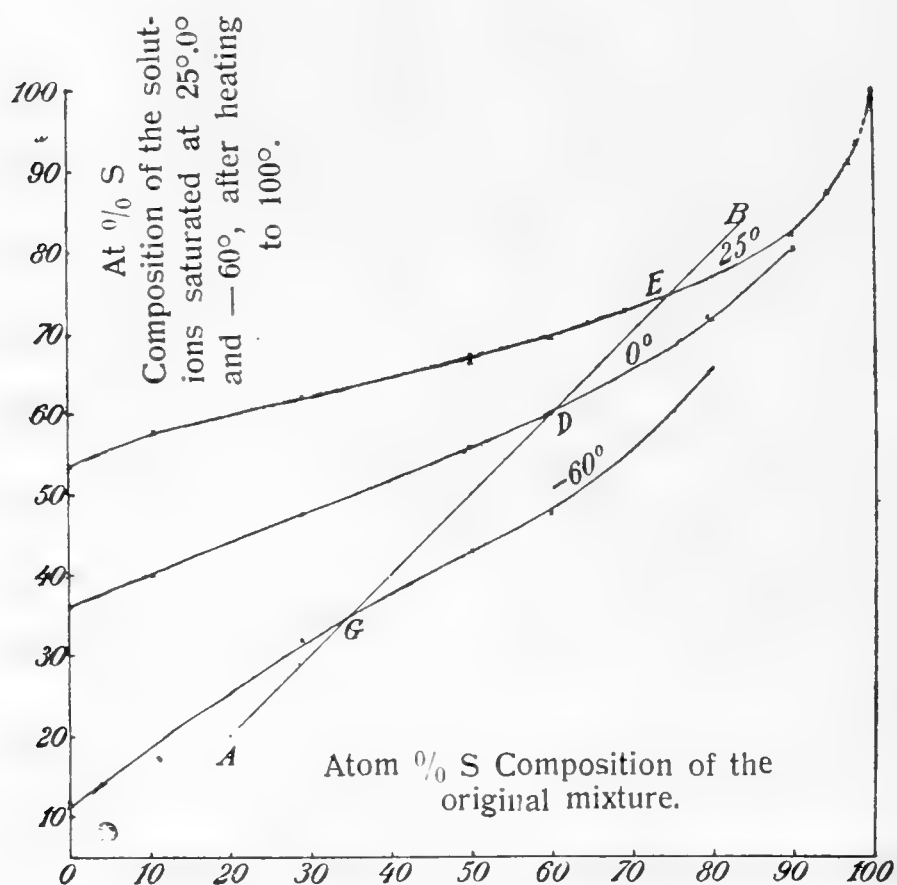


Fig. 4.

If we represent graphically the relation between solubility and original composition we obtain the lines shown in Fig. 4.

A comparison of these lines with those of Figs. 2<sup>b</sup> and 3<sup>b</sup> shows that they correspond with the lines of Fig. 3<sup>b</sup> which are drawn in case a new modification is present. The solubility line for  $25^\circ$ , in particular, proceeds very distinctly towards 100 at % of S.

In the second place, mixtures of varying composition were heated

TABLE II.

Original composition in <i>at. % S</i>	Composition of the solutions saturated at 25° in <i>at. % S</i> , after heating to			
	50°	75°	100°	125°
0	53.5	53.5	53.5	53.5
10.0	57.2	57.9	57.6	57.9
28.7	—	—	62.0	—
30.9	60.7	61.5	—	63.2
50.3	63.2	64.4	—	67.6
60.1	65.0	66.7	—	71.3
69.1	66.6	70.9	72.8	74.1
81.4	70.6	—	—	—
83.7	—	75.0	—	80.1
89.9	—	—	82.1	—
94.6	—	—	87.7	—
94.9	—	—	—	91.5
96.8	—	—	—	93.6
97.4	—	—	91.0	—
98.0	—	—	93.5	—
98.1	—	—	—	95.6

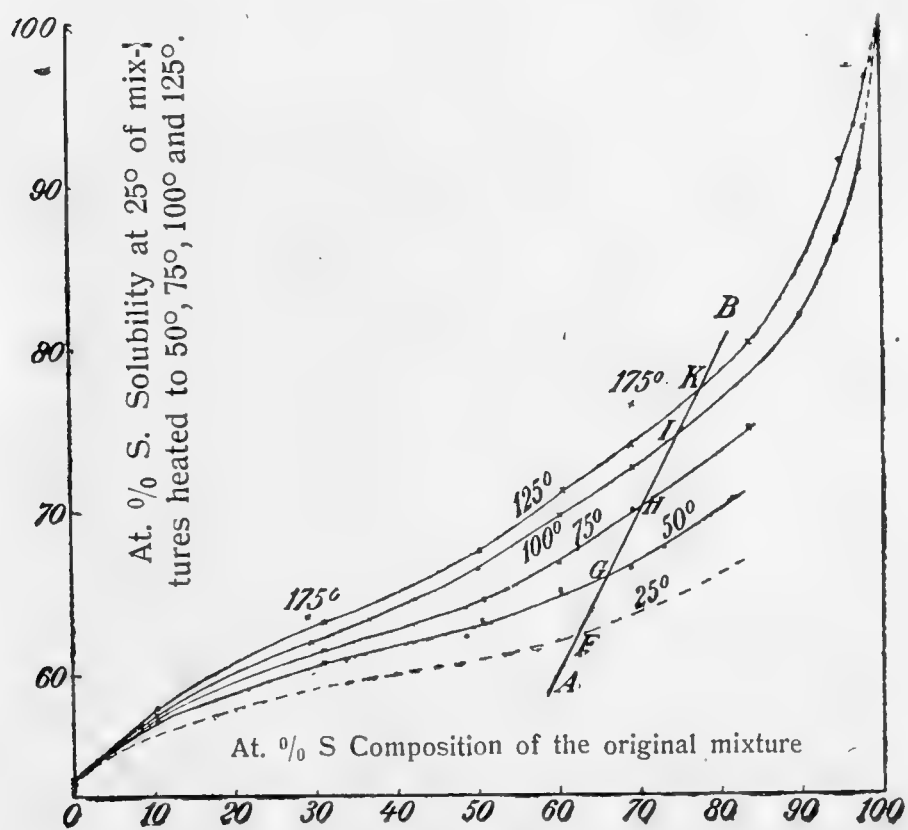


Fig. 5.

to 125°, 100°, 75° and 50° and the solubility determined at 25°. The values found are given in table II.

From the line of 125° we see, still more distinctly than from that at 100°, that this proceeds towards 100 at. % S in accordance with the line deduced in case a new modification is formed.

No experiments could be carried out with quantities of sulphur larger than indicated in the table. Not at 50° and 75° because the liquid at these temperatures was not homogeneous. Not at 100° and 125° because the liquids rich in sulphur are very viscous and, therefore, cannot be separated from the crystals by centrifugal action.

The line drawn for 25° has not been determined experimentally, but has been found by extrapolation of the values at 50°, 75°, 100° and 125°. We notice from this line that even at 25° a considerable amount of the new sulphur form must be present. A comparison of the lines for 25°, 50°, 75°, 100° and 125° shows that the quantity of the new modification increases at a higher temperature and that this increase for each 25° difference, is greatest below 100°; from 100° to 125 the solubility increases but little. For this reason, when the liquids are heated at 175°, we find but a small increase in solubility, as shown by the two points drawn in Fig. 5. We must, however, bear in mind that at 175°, the equilibrium will not be fixed. If such were the case a somewhat greater solubility would have been found.

The existence of a new modification of sulphur, has not, however, been proved with absolute certainty by the course of the lines in Fig. 5. It might yet be possible that a compound was formed very rich in sulphur, such as  $S_{16} \cdot S_2 \cdot Cl_2$  which contains 94 at. % of sulphur. In such case the existence of these liquids rich in sulphur would be explained. The line in Fig. 5 then ought not to proceed in the extrapolated part towards 100 at. % of S, but turn to the right and attain say at 96 or 98 at. % of S their limitation value.

That, however, a new modification is actually formed is shown in the following manner.

When in mixtures of sulphur and sulphur chloride a new modification is formed on heating, this must also be the case with pure sulphur although perhaps in smaller quantities than in mixtures with  $S_2Cl_2$ . Moreover it may be — and there is reason to suppose so — that the conversion of the new modification into  $S_8$ , or reversely, proceeds more rapidly when no or little  $S_2Cl_2$  is present. This might be the reason why the formation of that new modification in pure sulphur could not be demonstrated.

We have succeeded however, in demonstrating that the new modification is formed in pure sulphur also. When sulphur is heated to  $125^{\circ}$ , rapidly poured out and powdered and then placed into  $S_2Cl_2$ , the solubility is larger than that of rhombic sulphur alone.

In this way was found :

1. Sulphur after heating to  $125^{\circ}$  and rapid cooling mixed with  $S_2Cl_2$  to 69.2 at. % of S. Solubility = 56.0 at. % of S.
2. Id. Mixed with  $S_2Cl_2$  to 73 at. % of S. Solubility = 56.5 at. % of S.
3. Id. Mixed with  $S_2Cl_2$  to 80.9 at. % of S. Solubility 58.5 at. % of S.

The solubility at  $25^{\circ}$  for sulphur, which has not been heated, is only 53.5 at. % of S. The heated sulphur has, therefore a considerably larger solubility than the non-heated rhombic sulphur, which proves that in the heated sulphur another modification is also present. It has already been explained above that this cannot be amorphous sulphur. But it is also shown by the fact that the sulphur content of the saturated solutions is all the greater when more sulphur is added. Now, the solutions 1—3 indicated above are all saturated with amorphous sulphur for this was present in large excess. If now the increase in solubility were caused by the amorphous sulphur getting dissolved, the solubility from 1—3 ought to be the same. To make more sure, the solubility of a mixture of rhombic and amorphous sulphur at  $25^{\circ}$  was determined also. For this was found 54.5 at. % of S. Even after 24 hours the solution was still somewhat turbid owing to amorphous S. The figure 54.5 at. % of S is therefore too high. Hence, it appears again that the solubility of amorphous sulphur is very slight and cannot explain the increase of solubility in experiments 1—3.

In connection with his theory of allotropy, Prof. SMITS has pointed out, that the system sulphur must be a ternary system. The possible relation between the sulphur modification we were dealing with, and that assumed by Prof. SMITS, will be discussed in a following paper, as well as the results of investigations on the molecular weight and the permanency of the modification, which are now being carried out.

*Amsterdam, Chem. Lab. University.*

August 1912.

**Chemistry.** — “*On the relation between the sulphur modifications.*”

By DR. H. L. DE LEEUW. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of September 28, 1912).

Prof. SMITS has authorised me to criticise a recently published report of a lecture by KRUYT delivered before the Deutsche Bunsen Gesellschaft (*Z. f. Elektr. Chem.* 1912, 10, 581) and to make use for this of the experimental data obtained during a research conducted by me as private assistant. Before proceeding to this it seems to me desirable to mention very briefly some points in historical order.

SMITH and his coadjutors were the first to assume dynamic isomery with sulphur. They determined the course of the equilibrium line  $S_\lambda - S_\mu$  and also the solidification line of the monoclinic sulphur. KRUYT, in addition, determined the initial melting points of rhombic sulphur which, at different temperatures, had got into equilibrium with  $S_\mu$ , the melting point line of SMITH being used as the method of analysis. Moreover, he concluded to the existence of a metastable region of demiscibility contrary to SMITH and his co-workers who rejected this.

By Prof. SMITS it was pointed out already in 1910 that the results of the sulphur investigation contain data which support his theory of allotropy. KRUYT, for instance, had stated that when starting with rhombic sulphur, which has placed itself in equilibrium at  $90^\circ$  and then determining the melting point of the sulphur in this condition, according to SOCH'S method,  $110^\circ.9$  was found whereas, in the same method of working, a melting point of  $111^\circ.4$  was observed when the  $S$  had come into equilibrium at  $65^\circ$ . From this result it, of course, follows that we are dealing here with an inner equilibrium in the solid state, therefore with mixed crystals, and that the line for the inner equilibrium in the solid condition proceeds on increasing the temperature, to a greater  $S_\mu$  content, as in the liquid. Prof. SMITS therefore changed the  $T, x$ -figure (fig. 1) into that indicated in fig. 2.

Afterwards, A. SMITH and CARSON (*Z. f. phys. Chem.* 1911, **77**, 661) have determined the solidification line of  $S_{Rh}$  also making use of the lines determined previously. This line differs a little with the curve of KRUYT. Moreover, they also found a third melting point line, that of the “soufre nacré”. In the same time KRUYT (*Chem. Weekblad* 1911, 647) announced that all the values of the transition temperature ( $T \rightarrow$ ), with varying quantities of  $S_\mu$  are situated lower than REICHER'S value ( $95^\circ.6$ ) and also that the dimensions of the mixed crystal-region are not such that the influence thereof on his calculations exceeds the experimental errors.

In the meanwhile it had been pointed out by Prof. SMITS that the theory of the allotropy leads us to expect that the previous history

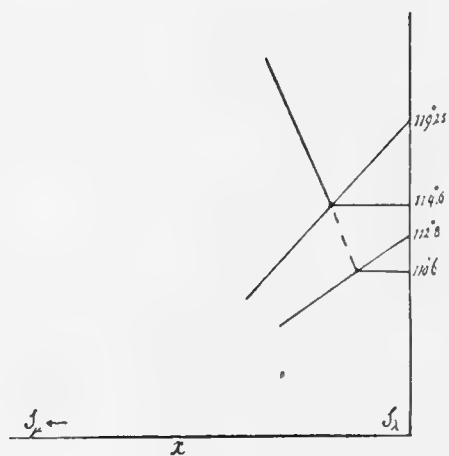


Fig. 1.

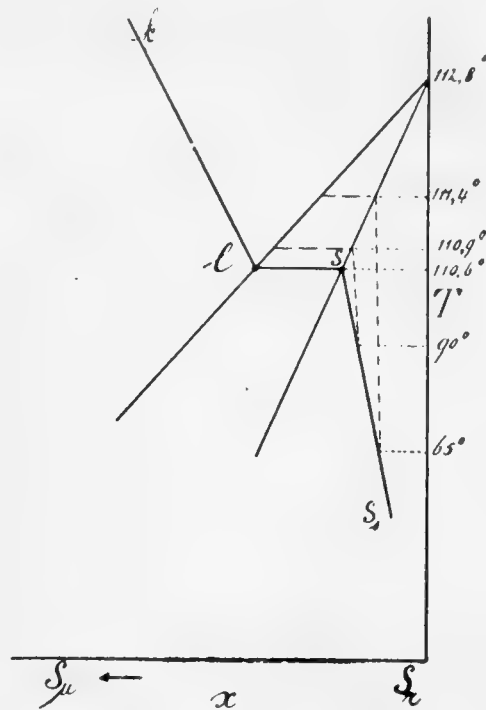


Fig. 2.

might exert an influence on the situation of the transition point. Specially conducted experiments confirmed this surmise completely (A. SMITS and H. L. DE LEEUW, On the system sulphur, Proc. 1911). The  $T \rightarrow$  was determined according to REICHER'S method with this modification that the upper end of the dilatometer was not sealed. The transition temperature was consequently determined at 1 atm. pressure, whereas with REICHER the pressure amounted to 4 atm. The influence which the pressure exerts on the transition temperature is calculated by REICHER to be equal to  $\frac{1}{20}^{\circ}$  rise per atm. pressure increase. This tallies, as instead of  $95^{\circ}.6$  observed by REICHER, I found  $95^{\circ}.45$ .

Now in order to find  $T \rightarrow$  when  $S_{\mu}$  was present the sulphur was heated to boiling in the dilatometer and then rapidly cooled so that a great part of the  $S_{\mu}$  formed remained intact. Then the dilatometer liquid (a mixture of 9 vol. of turpentine and 1 vol. of  $CS_2$  which had been boiled for a long time with sulphur and showed no longer an evolution of gas) was added and the transition point determined by ascertaining at which temperature one was *above* and when one was *below*  $T \rightarrow$ . In the first case the level of the liquid rises at a constant temperature (conversion  $S_{Rh} \rightarrow S_M$ ), in the second case it falls (conversion  $S_M \rightarrow S_{Rh}$ ).

Here it was shown that already at a much lower temperature than

95°.45 could be observed a conversion of rhombic into monoclinic sulphur, which could be made reversible by lowering the temperature; hence there must be a transition point. A conversion of  $S_\mu$  into crystalline  $S$  could not account for that reversible behaviour as then either  $S_M$  or  $S_{Rh}$  was formed owing to which the volume ought to always decrease and no temperature should be found at which the volume increased. As stated in the communication from Prof. SMITS and myself, the  $S_\mu$  present in the mixed crystals will be converted *continuously* into  $S_i$ , from which it follows that when an increase in volume is noticed, the conversion  $S_{Rh} \rightarrow S_M$  predominates<sup>1)</sup>. So as to make sure that the phenomena observed were not due to the not yet complete equalization (after about 10 minutes) of the each time differently chosen temperature of the thermostat, a second dilatometer containing  $S$  which had been in equilibrium for weeks and gave a  $T \rightarrow$  of 95°.45 was placed in these experiments, by way of a check, next to the dilatometer, which contained sulphur with much  $S_\mu$ . Below follows with full details the result of one of the experiments. In the first column is given the temperature of the thermostat. The second column gives the time elapsed after placing the dilatometer in the thermostat. In the third column is found, first the change in the dilatometer with the  $S_\mu$  and below that in the control dilatometer.

From this we see that 2<sup>1</sup>/<sub>4</sub> hours after the heating the control dilatometer at 71° did not further rise in 15 minutes, but the other one did, showing that a conversion took place with change in volume, which can never be explained by conversion of  $S_\mu$  into  $S_{Rh}$  or  $S_M$  as this causes the volume to decrease. The only possible thing, therefore, is that  $S_{Rh} \rightarrow S_M$ , that is to say the transition point has been lowered by  $S_\mu$  to below 71°. This fall depends on the quantity of  $S_\mu$  which will decrease gradually. The processes which take place in presence of each other are  $S_\mu \rightarrow S_{Rh}$ ,  $S_\mu \rightarrow S_M$  and  $S_M \rightleftharpoons S_{Rh}$ . The decrease of  $S_\mu$  may be seen from the rise in  $T \rightarrow$ . After 4<sup>1</sup>/<sub>1</sub> hours, no more change in volume at 71° could be observed, whilst after 6<sup>2</sup>/<sub>2</sub> hours the liquid in the dilatometer distinctly fell. The transition temperature then appeared to lie between 71° and 72°<sup>2)</sup>. In this way

1) The forming or augmentation of a second phase rich in  $S_\mu$  should also cause the volume to increase. Whether a part of the depression in this manner has to be explained, is on trial. It is however sure, that even when it were so, the lowering of the transition point by  $S_\mu$ , has to be considered as certain.

2) This is not quite correct on account of the always continuing conversion  $S_\mu \rightarrow$  crystalline  $S$  in consequence of which, on decrease of the volume, a slight conversion of  $S_{Rh} \rightarrow S_M$  can take place. For the sake of brevity we will disregard this, however.



Temperature of bath	Total lapse of time after placing in the thermostat	Rise in mm.	Time in which the rise was observed.
71°	2 $\frac{1}{4}$ hours	+2 0	15 min.
	4 $\frac{1}{4}$ "	0 0	10 "
	6 $\frac{1}{2}$ "	-1 $\frac{1}{2}$ 0	12 "
76°	23 $\frac{1}{2}$ "	+1 $\frac{1}{2}$ 0	after 12 m. 10 "
78°	24 $\frac{1}{4}$ "	+2 $\frac{1}{2}$ 0	after 15 m. 12 "
	24 $\frac{3}{4}$ "	+3 $\frac{1}{2}$ 0	20 "
	28 "	+1 $\frac{1}{2}$ 0	18 "
	29 "	+1 $\frac{1}{2}$ 0	15 "
	29 $\frac{3}{4}$ "	-1 $\frac{1}{2}$ 0	12 "
	47 $\frac{1}{2}$ "	-2 $\frac{1}{2}$ 0	15 "
86°	48 $\frac{1}{2}$ "	-1 0	after 12 m. 15 "
86°	49 $\frac{1}{4}$ "	+2 0	after 15 m. 10 "
87.5°	52 "	+2 $\frac{1}{2}$ 0	12 "
	53 $\frac{1}{2}$ "	+1 0	10 "
	72 "	-2 0	10 "
91.5°	73 "	+1 0	after 14 m. 12 "
	73 $\frac{1}{2}$ "	+1 0	18 "
	75 $\frac{1}{4}$ "	0 0	15 "
	76 $\frac{1}{4}$ "	-1 0	18 "
	78 "	-2 0	15 "
94°	78 $\frac{1}{2}$ "	+1 $\frac{1}{2}$ 0	after 12 m. 20 "
	168 "	-1 $\frac{1}{2}$ 0	25 "
95.2°	168 $\frac{1}{2}$ "	+1 0	20 "
	169 "	+1 0	22 "
95.3°	169 $\frac{1}{2}$ "	somew. falling 0	14 "
95.4°	169 $\frac{3}{4}$ "	0 0	12 "
	170 "	0 0	12 "
95.6°	170 $\frac{1}{4}$ "	+1 $\frac{1}{2}$ 0	18 "
	172 "	+1 +1 $\frac{1}{2}$	20 "

the rise of  $T \rightarrow$  could be readily traced, from which it appeared that this, with ever decreasing velocity, rose until  $95.45^\circ$  was reached, which temperature is the true unary transition temperature. Hence, we see that  $T \rightarrow$  can be lowered by  $S_\mu$  fully  $20^\circ$ . In harmony therewith is also the fact that starting from  $S_\mu$ -free sulphur, REICHER (Dissertation) obtained, as he thought, diverging results, namely first a transition temperature of  $97^\circ$  which temperature he found in course of time on the decrease until the unary transition temperature  $95^\circ.45$  was reached at which  $S_\mu$  is present.<sup>1)</sup>

Simultaneously with the result mentioned above several experiments were communicated which contrary to KRUYT's investigation (Z. f. phys. Ch. **64** 513) removed all grounds for the assumption of a metastable region of demiscibility in the pseudo system. It appeared that the occurrence of two layers is due to the difference in temperature which between the two layers may amount to even from  $10$  to  $30^\circ$ . When the heat conductivity was improved by the introduction of platinum wire or small gauze this phenomenon occurred less distinctly or not at all. Quite in harmony therewith is also the influence which an alteration in the diameter of the sulphur tubes exerts on the appearance of two layers. That we are not dealing here with a metastable region of demiscibility appeared, contrary to KRUYT, also from the fact that in the presence of  $\text{NH}_3$ , which is a positive catalyst, that apparent unmixing occurred still better, notwithstanding we now follow the equilibrium line. While KRUYT believed that there existed a constant three-phase temperature  $S_\mu$  with two liquid layers at  $110^\circ$  (intersecting point of the solidifying line of  $S_M$  with the region of demiscibility, point  $d$  of Fig. 4), this also did not prove correct as, on inoculation with monoclinic sulphur, solidification temperatures of  $108^\circ$  and  $109^\circ$  were observed and, when starting from pure  $S_\mu$ , even  $106^\circ$ .

As the last publication I mention KRUYT's lecture which contains pretty well the same as the article in the Chem. Weekblad except that Fig. 3 occurs also.<sup>2)</sup> From this we notice that KRUYT now assumes that  $C$  ( $T \rightarrow$  of  $S_\mu$ -free sulphur) lies at  $94^\circ.8$ , GH at  $95^\circ.6$  (unary temp. really  $95^\circ.45$ ). In what manner these experiments have been carried out, is, however, not communicated. They must be faulty or

<sup>1)</sup> GERNEZ also gives too high values ( $97^\circ.6$ — $98^\circ.4$ ). As GERNEZ only observed  $SRh \rightarrow SM$  and not  $SM \rightarrow SRh$  his figures are likely to be too high and do not prove much.

<sup>2)</sup> In the Fig. KRUYT draws the  $S_\mu$  to the right. The reason that I always place it to the left is that I do not want to depart from the custom to place the substance with the lowest m.p., therefore, presumably  $S_\mu$ , to the left.

interpreted wrongly for it is a fact that addition of  $S_\mu$  lowers the transition point. The highest point given by KRUYT for the metastable equilibrium  $S_R \rightleftharpoons S_M$  is  $96^\circ$ . Above this,  $S_R$  when passing into  $S_M$ ,

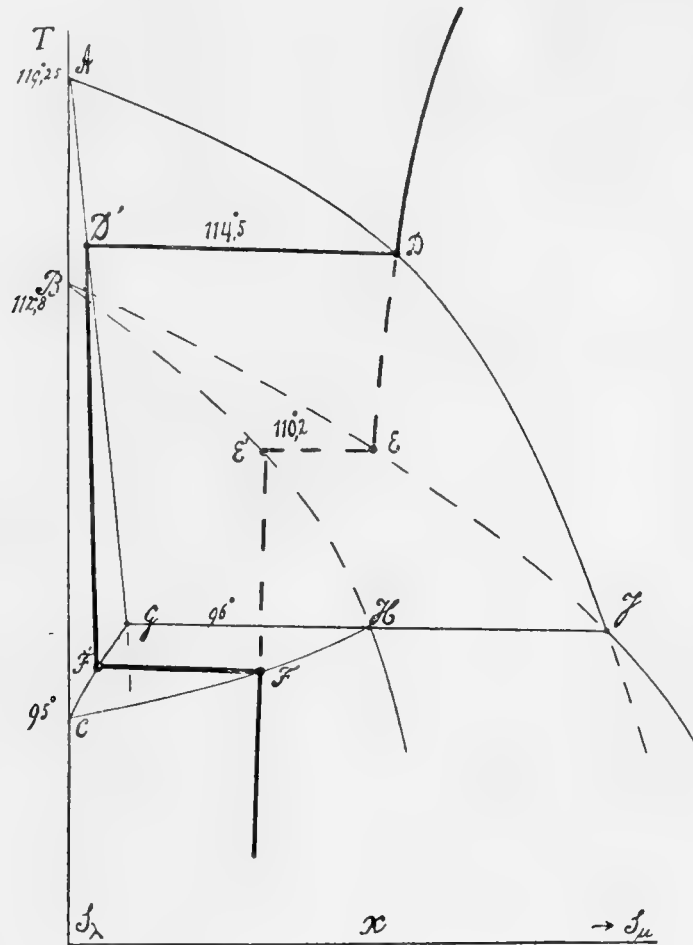


Fig. 3.

ought to begin to melt. This statement is rather remarkable when we read that KRUYT in the Chem. Weekbl. 648, (1911) actually states that all values for the  $T \rightarrow$ , on change of  $S_\mu$ -content, lie *lower* than  $95^\circ.6$ . I should like to ask, how that temperature has been found? Also, the high values ( $97^\circ.6$  and  $97^\circ$ ), determined by GERNEZ and REICHER, find no room in KRUYT's Figure.

Hence, it is faulty without any doubt to let  $CG$  proceed to higher temperatures; this line falls. If, however, we draw  $CG$  sinking we obtain a Figure which is identical with a figure previously given by Prof. SMITS (Proc. 1911, 264) and represented here by Fig. 4. This identity becomes perfect if we leave out the dissociation region drawn therein (which as stated in a note ought to be discarded as not a single experimental fact points to its existence). In this way we obtain Fig. 5. What KRUYT (fig. 3) calls  $CG$  is in fig. 4 and 5 *op* etc.

The deduction of the transition point of the sulphur with the aid of the equilibria lines of the solid substance is therefore not due to KRUYT.

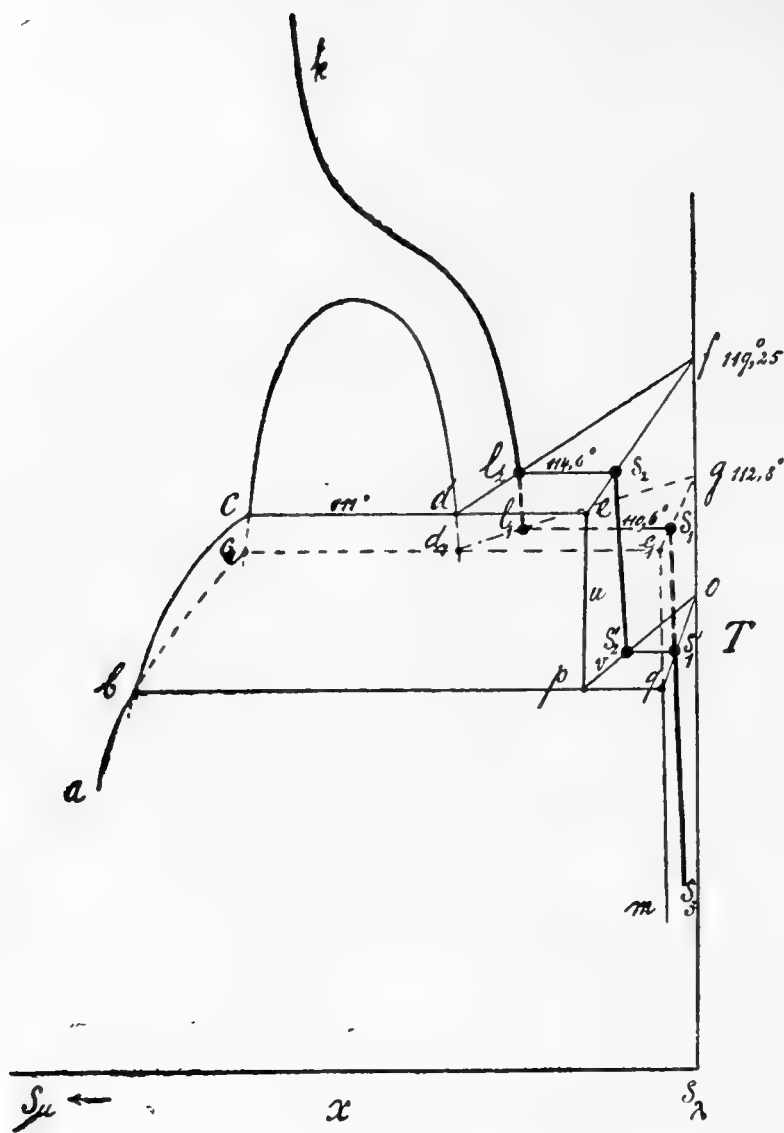


Fig. 4.

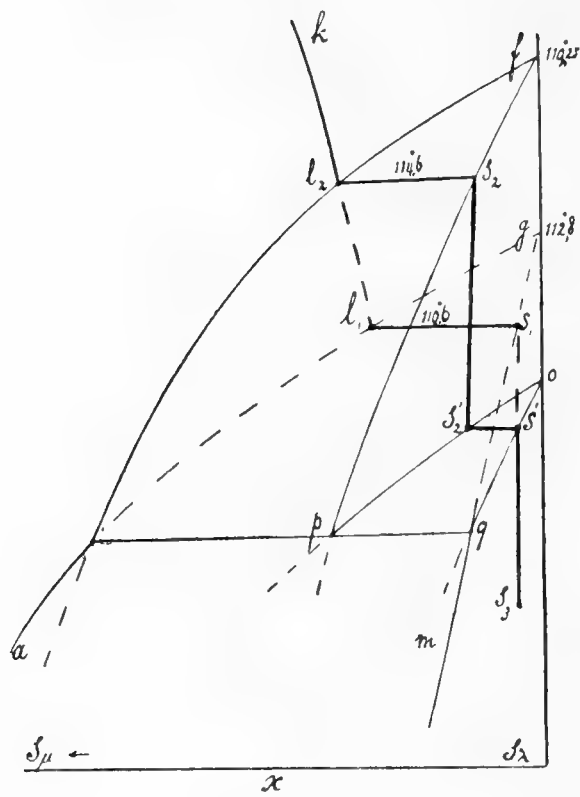


Fig. 5.

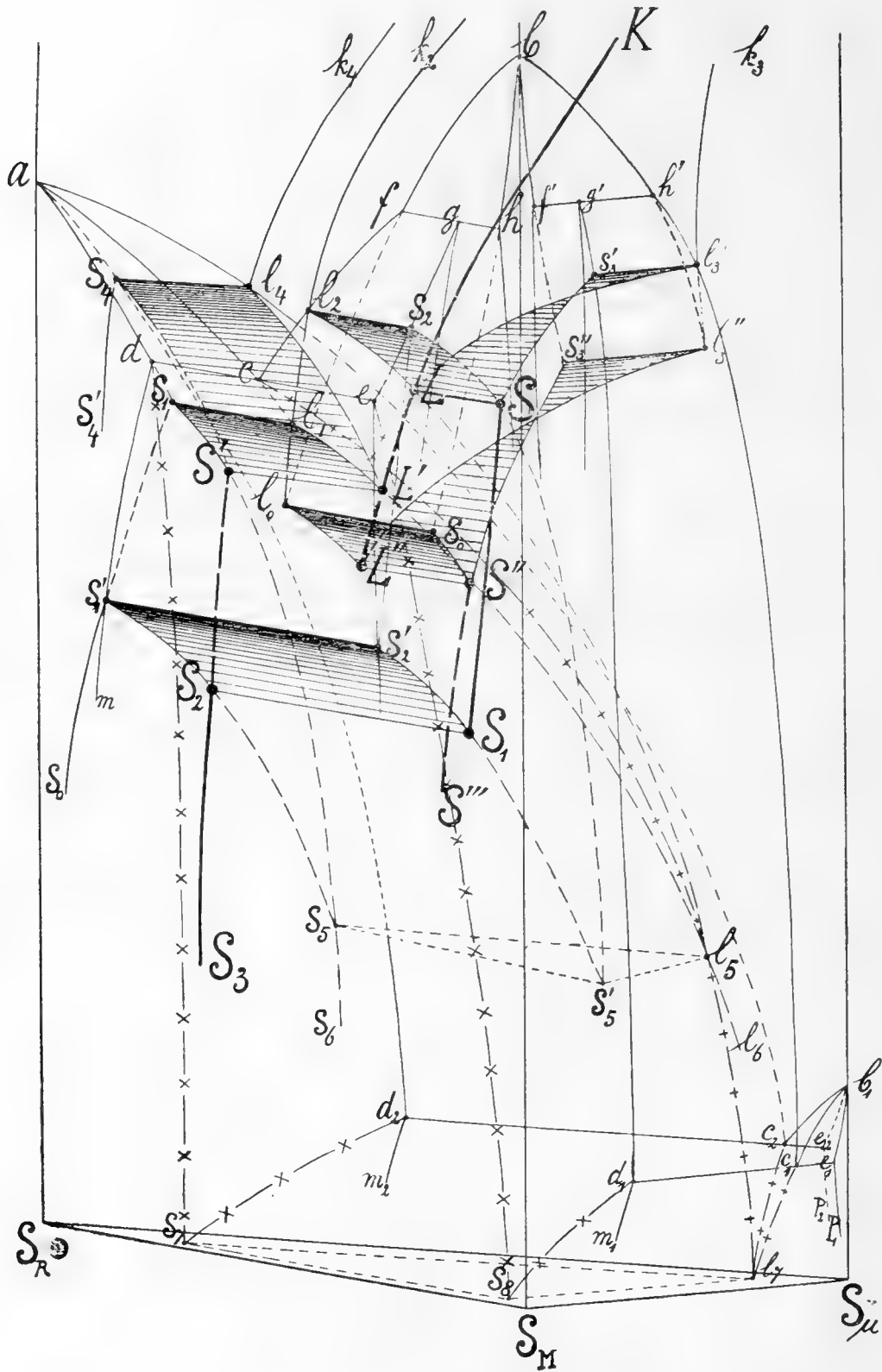
KRUYT draws no region of demiscibility, but states that for *the sake of brevity he discards the probable occurrence of the region of demiscibility*. It would have been more correct to state that *nothing pleads for its existence and that therefore it was omitted*. In connection herewith I will observe the following. If we prolong the lines  $AD$  and  $BE$ , as indicated by KRUYT (Zt. phys. Chem. 64, 513) they intersect each other at about  $106^\circ$ , so far above  $96^\circ$ .  $GHI$  would then lie at  $106^\circ$  which cannot be. If now we call to our aid a region of dissociation (see Fig. 2) this difficulty, of course, does not occur, but this alone does not justify the assumption of a region of demiscibility, particularly if we remember that the mode of representation is not correct.

The matter may indeed be explained readily when, as required by Prof. SMITS's theory, we not merely assume two kinds of sulphur  $S_\lambda$  and  $S_\mu$ , but (at least) *three* kinds of molecules which we will indicate briefly by  $S_\mu$ ,  $S_M$ , and  $S_{Rh}$ . Because there exists a transition point  $S_M \rightleftharpoons S_{Rh}$  we must also assume a pseudobinary system  $S_{Rh}-S_M$ . The whole  $S$ -diagram then becomes ternary of which already a schematic figure has been constructed (Proc. XIV, 266) Prof. SMITS has now modified the former ternary figure by omitting the region of demiscibility and keeping account with the third crystallised modification, the *soufre nacré*<sup>1)</sup>. This drawing is given in Fig. 6. The above mentioned difficulty does not arise here at all. The lines  $AD$  and  $BE$  from Fig. 3 are lines which in the ternary figure run over the surfaces  $l_2S_2LS$  and  $l_1S_1L^1S^1$  and therefore are spacial curves which may deviate much from the right ones. If we assume that the equilibrium  $S_M \rightleftharpoons S_{Rh}$  sets in with infinite velocity there is formed from the pseudo ternary figure the pseudobinary Fig. 5, in which the curves just mentioned have undergone an intricate projection, whereby a *crossing* may turn into an *intersection* so that the above mentioned intersection at  $106^\circ$  need not signify anything.

Hence, it is incorrect to assume, as KRUYT, SMITH, and others, that we can deduce from the unary solidification temperature of the  $S_{Rh}$  the  $S_\mu$ -content with the aid of the line of equilibrium, since in the projection the situation of the lines in regard to each other is totally changed. Also it is not permissible, as KRUYT has done, to first determine the melting point of the rhombic modification and then to determine the composition with the aid of the melting point when the substance has become monoclinic, for  $AD$  and  $BE$  need not, of course, be situated in *one* plane. KRUYT's experiments on the melting point of rhombic sulphur clearly indicate this.

<sup>1)</sup> See These Proceedings XV p. 369.

KRUYT has, in fact, not determined  $BE$ , but  $BE'$ , that is to say the *initial temperatures of fusion*<sup>1)</sup>. The line  $BE$  has been determined



<sup>1)</sup> He says, for instance, in his dissertation p. 48, of a mixture that at  $112^{\circ}.4$  it *just* commenced to melt and then takes that temperature as melting point temperature.

by SMITH; it differs somewhat and ought to lie somewhat higher<sup>1)</sup>. Now, KRUYT allows the sulphur to become monoclinic and then again determines the initial melting point, but according to his figure, this is totally impossible, when we notice that  $BE'$  is situated nearly totally between  $AD'G$  and  $ADJ$ , so that, starting from points of  $BE$  we arrive into the region monoclinic sulphur-liquid, owing to which the substance must be partly melted and consequently no initial melting point can be observed.

This is the result of the incorrect assumption that  $CG$  rises, owing to which  $AG$  nearly always gets situated quite to the left of  $BA$ . If  $CG$  is drawn falling (lowering of the transition point) in which case we again obtain Fig. 5 this difficulty does not arise.

Summarising, I arrive at the following conclusions which differs case we from that of KRUYT:

1<sup>st</sup> The modifications introduced by KRUYT in the previous Fig. of Prof. SMITS (Proc, XIV, 264) are incorrect.

2<sup>nd</sup> By addition of  $S_{\mu}$  the transition temperature  $S_{\mu} \rightleftharpoons S_{Rh}$  is lowered.

3<sup>rd</sup> Fig. 3 (from KRUYT) is not in harmony with the phenomena observed (also see ad 7). Even KRUYT's own experiments are in disaccordance with it.

4<sup>th</sup> KRUYT has determined not the line  $BE$  from Fig. 3, but the line  $BE'$ .

5<sup>th</sup> The system sulphur is not pseudobinary, but at least pseudo-ternary.

6<sup>th</sup> In consequence of this, the true direction of the lines from figs. 3, 4, and 5 is another one than that assumed by KRUYT. The significance of the intersecting points of the lines drawn by KRUYT also differs from that attributed to them by that investigator.

7<sup>th</sup> There exist no grounds for the assumption of a region of demiscibility.

*Inorg. Chem. Lab. University.*

*Amsterdam, September 1912.*

1) The difference has to be explained by the different method of working. Freezing points are easily found too low, melting points too high especially in the case of mixed crystals.

**Chemistry.** — “*On the nitration of the chlorotoluenes*”. By Prof. A. F. HOLLEMAN and Dr. J. P. WIBAUT.

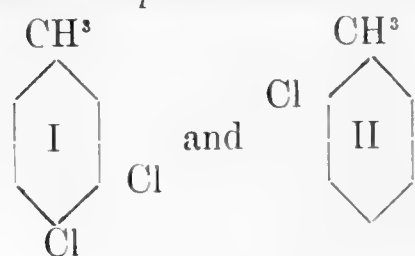
When two substituents are present in the benzene nucleus, both have a certain influence on the place where a third substituent enters. Which of the possible trisubstituted isomers will be obtained in a larger quantity depends, as I have shown elsewhere, on the velocity of substitution which both of the groups cause.

If we consider for instance a monochlorophenol, the new entering substituent places itself nearly exclusively on the ortho- and para-places with regard to hydroxyl and not on these places with regard to chlorine, because the velocity of substitution, which OH causes is much larger than that caused by chlorine.

By considering all the cases of substitution in the bisubstituted benzene derivatives, I found, that the velocity of substitution to meta-places is always much slower than that to para-ortho-places, and that the substituents that direct a new substituent to the latter places cause a velocity of substitution which decreases in the following order:



As the halogens and methyl cause no large difference in the velocity of substitution, it should be expected, that the entrance of a third group takes place para-ortho as well to the halogen as to methyl. Indeed, COHEN and DAKIN proved in an excellent and very laborious research that in the chlorination of orthochlorotoluene all the four possible chloro-*o*-chlorotoluenes are formed and in the chlorination of *p*-chlorotoluene the two possible dichlorotoluenes, whereas with



meta-chlorotoluene the same operation procured the isomers I and II, but not the symmetrical dichlorotoluene, just as might be expected, because neither chlorine nor methyl direct a substituent to meta-places.

In order to get an insight in the ratio of these velocities, it is necessary quantitatively to determine the proportions in which the isomers are formed; and as nitrations are generally not attended with production of secondary products, we resolved to study again the nitration of the monochlorotoluenes. Through former investigations it was known, that *o*-chlorotoluene yields the product  $\text{CH}_3, \text{Cl}, \text{NO}_2 = 1,2,5$  (GOLDSCHMIDT, HÖNIG, B. **19**, 2440), *m*-chlorotoluene yields the isomers  $\text{CH}_3, \text{Cl}, \text{NO}_2 = 1,3,4$  and  $1,3,6$  and para-chlorotoluene yields the isomers  $\text{CH}_3, \text{Cl}, \text{NO}_2 = 1,4,2$  and  $1,4,3$ . The latter nitration had been



already quantitatively studied in my laboratory by VAN DEN AREND, who had found that 58 % of the isomer 1,4,2 and 42 % of the other one (1,4,3) are formed.

As we supposed that the nitration of ortho-chlorotoluene would yield all the four possible mono-nitroderivatives, the first thing to do was to prove this. The nitration product presents itself as a yellow oil which commences to congeal only at about  $+1^{\circ}$ ; on the other hand, the eutectic temperature of the binary mixtures of the isomers  $\text{CH}_3, \text{Cl}, \text{NO}_2 = 1,2,3 + 1,2,4$  was found at  $8^{\circ}.2$ ; of  $1,2,3 + 1,2,5$  at  $+1.1$ ;  $1,2,4 + 1,2,6$  at  $17^{\circ}.2$ ;  $1,2,5 + 1,2,6$  at  $7^{\circ}.2$ . It was therefore evident, that the nitration product could not be a mixture of only two isomers, but must contain still a third and perhaps also a fourth. Of course, this conclusion only holds good, when the nitration product contains only the mononitrocompounds. This was proved to be so by fractional distillation and the determination of the refraction of the first passing drops and of the residue, which showed both the same refraction as the principal portion of the distillate.

As it proved to be impossible to separate the isomer nitro-*o*-chlorotoluenes themselves, we reduced them; the chlorotoluidine  $\text{CH}_3, \text{Cl}, \text{NH}_2 = 1,2,5$ , melting at  $81^{\circ}$ , separates easily in large quantities. The oily mixture which remains then was acetylated, because we stated that the acetylcompounds of the two vicinal chlorotoluidines  $\text{CH}_3, \text{Cl}, \text{NH}_2 = 1,2,3$  and  $1,2,6$  are sparingly soluble in cold benzene. Indeed, by treating the mixture of acetylcompounds with this solvent, these two isomers were easily isolated and identified; the presence of the isomers  $\text{CH}_3, \text{Cl}, \text{NO}_2 = 1,2,3$  and  $1,2,6$  in the nitration product was thus proved.

It was far more difficult, to prove also the presence of the fourth isomer 1,2,4. After about six months of strenuous labour, in which a great many methods were tried, we succeeded at last in the following way: about 100 grams of the nitration product was reduced. After separation of the isomer 1,2,5, the residue was acetylated and the vicinal isomers isolated by treatment with benzene. The products that remained in the benzenic solution were saponified; from the mixture of chlorotoluidines so obtained, a great deal of the isomer 1,2,5 separated again on cooling. The liquid residue, again converted into acetylcompounds, yielded again on treatment with benzene a considerable portion of the vicinal compounds. After all these operations, there remained about 9 grs. of a mixture of acetamino-2-chlorotoluenes, in which the compound 1,2,4 must be accumulated. By dissolving this mixture in a little quantity of benzene and by fractional precipitation of this solution with petroleum

ether, the first fractions are still essentially the isomer 1,2,5; but at last, a fraction was obtained, melting at  $70^{\circ}$ — $75^{\circ}$ , whose melting point rose to  $95^{\circ}$ , when it was mixed with an equal quantity of the acetaminocompound 1,2,4. Though the latter could not be isolated in a perfectly pure state from the mixture, this test proves nevertheless with certainty its presence. This was still corroborated by treating an artificial mixture of the four isomers, containing them in nearly the same proportion as the nitration product (see below) in the same way; it showed quite the same peculiarities and neither from this mixture could the isomer 1,2,4 be isolated perfectly pure. The proportions of solubility of this compound and of many of its derivatives in comparison with those of the isomers are too unfavourable to allow its extraction.

After having proved that really the four possible nitro-*o*-chlorotoluenes occur in the nitration product of *o*-chlorotoluene, we proceeded to estimate the relative quantities in which these isomers are formed. The nitration itself was executed as follows. To 10 gr. *o*-chlorotoluene was dropped 40 grs. of nitric acid sp.gr. 1.52 while stirring mechanically; the temperature being kept between  $-1^{\circ}$  and  $+1^{\circ}$ .

For the analysis of the nitration product, the melting point method was applied in the modification described by VALETON. When looking at the six binary melting curves, which are possible with the four isomeric nitro-*o*-chlorotoluenes, one perceives, that these curves coincide over a considerable range of temperature. For instance, considering the binary curves for 1, 2, 5 + 1, 2, 3 and 1, 2, 5 + 1, 2, 4, we see that the branches at the side of the isomer 1, 2, 5 coincide practically, and it is the same in the other cases. We have then to do with so called "ideal melting curves"; they show the property that the lowering of the freezing point, say of the isomer 1, 2, 5, is the same for the addition of a certain percentage of any of the other isomers or of mixtures of them, unless their sum comes again to the same percentage.

Wishing now to determine quantitatively one of the isomers, say 1, 2, 5, we add to a known weight of the nitration product so much of that isomer (of course also weighed) that it crystallizes at the first freezing point of the mixture and we determine this point. We find then with the aid of one of the melting-point curves the total amount of this isomer in the mixture and it is now only a simple arithmetic operation to calculate the amount of the isomer in the original nitration product. In the same way, the quantity of the other isomers is determined.

By this method, we found that the nitration product of *o*-chloro-

toluene contains:

Isomer	1, 2, 5	1, 2, 4	1, 2, 6	1, 2, 3
%	43.3	17.0	20.5	19.2

in which the figure for 1, 2, 3 is obtained by subtraction. It may be observed, that this method of analysis was first tried with good result on artificial mixtures of the four nitro-*o*-toluenes.

For the application of this method of quantitative analysis, it is necessary to possess the isomers present in the nitration product in a perfectly pure state. This presented some difficulty with the nitration product of *m*-chlorotoluene, the nitro-*m*-chlorotoluenes being hardly known and surely not obtained chemically pure until now. I shall not give a description of their preparation and purification here, but only mention that the isomer 1, 3, 6 ( $\text{CH}_3 = 1, \text{Cl} = 3$ ) solidifies at  $24^\circ.9$ , the isomer 1, 3, 4 at  $24^\circ.2$ , the isomer 1, 3, 2 at  $23^\circ.4$ , and the isomer 1, 3, 5 at  $58^\circ.4$ .

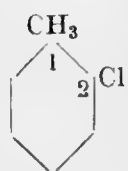
The quantitative nitration of *m*-chlorotoluene was executed in the same way as is described for *o*-chlorotoluene. By applying the method VALETON on the nitration product, we found for its composition the following figures:

Isomers	1, 3, 6	1, 3, 4	1, 3, 2
Percentage	58.9	32.3	8.8

The figure for the isomer 1, 3, 2 is the difference of the sum of the two isomers from 100, the method VALETON giving only more exact results as the quantities to be determined are larger. On the other hand however, we found by direct determination an amount of 8.3%. We believe it therefore proved with certainty that this isomer is present in the nitration product, and that the isomer 1, 3, 5 is not present in it in an appreciable quantity. The presence of the two other isomers was already known by an investigation of REVERDIN.

From the figures obtained in analyzing the nitration products of *o*-, *m*-, and *p*-chlorotoluene we may now draw the following conclusions.

In *o*-chlorotoluene, methyl directs the entering substituent to the places 4 and 6, chlorine to the places 3 and 5. They act therefore independently of one another, the little quantity of *m*-compound that is formed in the nitration of toluene being left out of consideration.



When the velocity of substitution, caused by methyl and chlorine were the same, the isomer nitro-*o*-chlorotoluenes would be formed in the same proportion as in the nitration of chlorobenzene on one

hand and of toluene on the other hand. It must only be taken into consideration that one of the ortho-places both of methyl and of chlorine is occupied and so the remaining *o*-places will be substituted in the same ratio as if both *o*-places towards CH<sub>3</sub> and Cl were free. One should therefore expect a ratio of the isomers as follows:

$$\frac{1, 2, 3 \quad 1, 2, 4 \quad 1, 2, 5 \quad 1, 2, 6}{30 + 2 : 38 : 70 + 2 : 58}$$

because the nitration of toluene gives 58% *o*-, 38% *p*- and 4% meta-compound and the nitration of chlorobenzene gives 30% *o*- and 70% *p*-chloronitrobenzene. Of course the 4% of meta-compound formed in the nitration of toluene, must be divided equally between the places 3 and 5.

I deduced however that chlorine causes a larger velocity of substitution than methyl. If we call the ratio of these velocities  $x$ , we find for the proportion in which the isomers must be formed:

$$\frac{1, 3, 2 \quad 1, 2, 4 \quad 1, 2, 5 \quad 1, 2, 6}{30x + 2 : 38 : 70x + 2 : 58}$$

With the same reasoning we find for the proportion in which the isomer nitro-*p*-chlorotoluenes must be formed:

$$\frac{1, 4, 2 \quad 1, 4, 3}{58 : 4 + 30x}$$



for also in this case methyl and chlorine act independently of each other.

Equalling these figures with those found by experiment, we get the equations:

$$30x + 2 : 38 : 70x + 2 : 58 = 19.2 : 17.0 : 43.3 : 20.5 \text{ and}$$

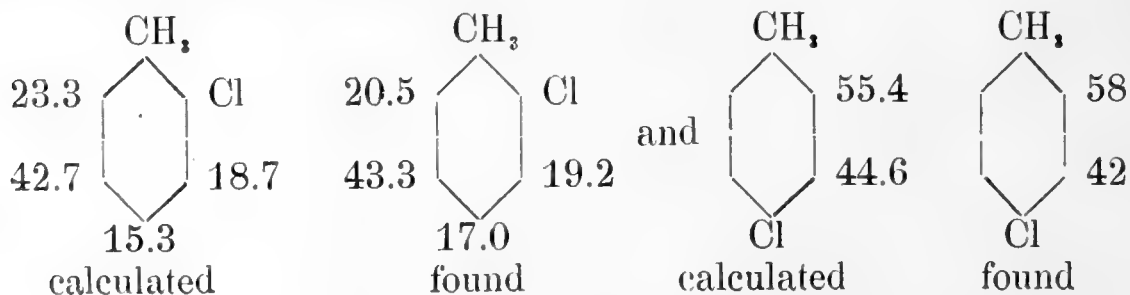
$$58 : 30x + 4 = 58 : 42$$

from which  $x$  may be calculated. As mean value of  $x$  we find in this way:

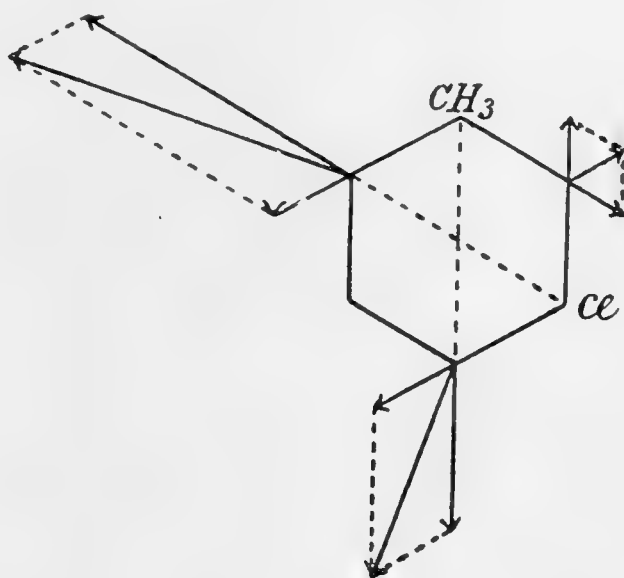
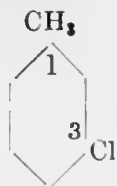
$$x = 1.491$$

expressing that chlorine causes a velocity of substitution 1.491 times as fast as methyl.

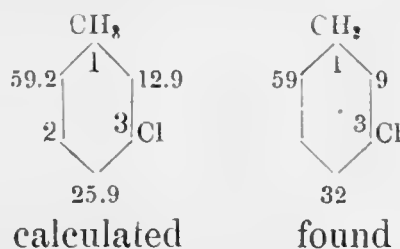
Calculating now with this value of  $x$  the proportion in which the isomers are formed, we get:



Calculating however with the same value of  $x$  the proportion of the nitro-*m*-chlorotoluenes formed by the nitration of *m*-chlorotoluene, there is no such gratifying concordance. This is due to the fact, that in this case the two substituents act no longer independently of each other, but that both methyl and chlorine direct the entering nitro group to the places 2, 4, and 6. Now we must not simply add the figures for the isomers, but we must take the resultant of their action, as is indicated in the scheme below, in which it is assumed that the benzene nucleus is a regular hexagon.



If we calculate in this way the proportion of the isomers, we find indeed a gratifying concordance between calculation and experiment:



*Amsterdam, org. chem. lab. of the Univ.*

October 1912.

**Physics.** — “*On the polarisation impressed upon light by traversing the slit of a spectroscope and some errors resulting therefrom.*” By Prof. P. ZEE MAN.

In a communication “The intensities of the components of spectral lines divided by magnetism”<sup>1)</sup>, I drew attention to the fact that by the polarizing action of the grating the ratio of the observed intensities of the components of a triplet differs considerably from

<sup>1)</sup> These Proceedings, October 26 1907.

the ratio present in the light as it is emitted by the source. In some cases the observer sees only a faint central component and two intense outer components, whereas the true ratio is just the reverse. In order to obtain in the image the true ratio of the intensities I suggested to introduce before the slit of the spectroscope a quartz plate of such a thickness, that the incident light is rotated through an angle of  $45^\circ$ .<sup>1)</sup>

Besides the mentioned polarizing effect of the grating there is a second cause tending to make the ratio of the intensities of components of different direction of vibration in the image different from that corresponding to the constitution of the emitted light. I mean the polarization impressed upon light which traverses fine slits. Since FIZEAU<sup>2)</sup> this effect is well-known, but the errors which may ensue from it in investigating spectral lines magnetically resolved have not yet been pointed out.

The following simple experiment is easily made. A vacuum tube charged with mercury is placed in a horizontal magnetic field. The emitted light is analysed by means of a spectroscope securing great illumination and high resolving power. The slit must be under the control of the observer at the eye-piece. The two yellow mercury lines, which are resolved into triplets or the green mercury line, which splits into three groups each of three lines may be observed. If the slit is rather wide then the central components of the yellow triplets may have twice the intensities of the outer ones; the three groups of the green mercury line have about the same integral intensity if not wholly resolved. If the slit (made of platinoid) be narrowed gradually, the intensity of all components decreases, but *that of the central component or group more than that of the outer ones*. At last the central components of the triplets and even the middle group of the brilliant green line can be *made to disappear entirely*<sup>3)</sup>, whereas the outer components remain visible. From these observations we cannot but conclude that the vibrations perpendicular to the slit at last hardly traverse the narrow slit.

The correctness of this explanation may be inferred from the fact that the *ratio* of the intensities changes gradually during the narrowing of the slit.

The view may be controlled by the following observations. If a

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<sup>1)</sup> l. c. p. 291.

<sup>2)</sup> FIZEAU. Ann. de Chim. et de Phys. Vol. 63 p. 385. 1861.

<sup>3)</sup> This extreme case involves the use of an exceptionally narrow slit rarely employed in practice.

quartz plate, rotating the plane of polarisation through  $90^\circ$  be introduced before the slit of the spectroscope, then only the outer components of the resolved spectral line can be made to disappear.

A second observation was made with the slit only of the spectroscope. The lens of the collimator being removed the slit of the spectroscope could be seen distinctly while viewing along the axis of the spectroscope. Looking through a calcspar rhomb the slit appears double. With a wide slit, illuminated by the radiating tube, the two images exhibit the same intensity; a narrowing of the slit gradually makes the image due to the vertical vibrations more brilliant than the other one.

I will mention two cases in which errors may be introduced by the polarization impressed by the narrow slit. This happens in the first place in the case mentioned above of the comparison of the intensities of resolved components vibrating in different planes. In the second place when the resolution of lines originally diffuse toward one side of the spectrum is investigated, *apparent* shifts and dissymmetrical separations may result. If the original spectral line is diffuse toward the red then a decrease of the intensity of the central line of a triplet will cause an apparent shift relatively to the outer components toward the violet. The reverse will be the case if the original line is diffuse toward the violet.

The apparent shift now under consideration has had no influence in the experiments concerning a change of wavelength by magnetic forces of the line Hg 5791, which the author<sup>1)</sup> and (independently) GMELIN<sup>2)</sup> discovered at the same time. Its existence could be demonstrated also by the method of FABRY and PEROT, a method not dependent upon the use of a narrow slit.

It is a favourable circumstance that a quartz plate introduced before the slit of the spectroscope and giving a rotation of the plane of polarization of  $45^\circ$ , eliminates at the same time as well errors due to the polarising action of the grating as those caused by the narrowness of the slit.

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<sup>1)</sup> ZEEMAN, Change of wavelength of the middle line of triplets. These Proceedings February 29, 1908, in print in the Dutch edition March 12, 1908, in the English March 29, 1908.

<sup>2)</sup> P. GMELIN. Über die unsymmetrische Zerlegung der gelben Quecksilberlinie 5790 im magnetischen Felde. Physik. Zeitschr. p. 212 (eingegangen 24 Febr. 1908) appeared April 1, 1908.

**Physics.** — “*Contribution to the theory of binary systems. XXI. The condition for the existence of minimum critical temperature.*”

By Prof. J. D. VAN DER WAALS.

Already in the theory of binary systems concerning perfectly miscible substances we repeatedly found the case of a minimum critical temperature, and already in my “*Théorie moléculaire*” I derived the condition for the existence of such a minimum, and expressed it in the form:

$$\frac{a_{12}}{b_{12}} < \frac{a_1}{b_1} \text{ and } \frac{a_{12}}{b_{12}} < \frac{a_2}{b_2}.$$

In my investigations of recent times, in which I chiefly intended to ascertain the conditions for the only partial miscibility, my attention was again directed to the possibility of the existence of a minimum  $(T_k)_x$ , and I have come to the conclusion that there is also question of such a minimum  $(T_k)_x$  for the mixture ether-water, but that the value of  $x$  for  $T_k$  minimum lies very close to the ether side. If as second component we always take the substance with the greater value for the size of the molecules, so ether in the case under consideration, the value of  $x$  is 1 or nearly 1. In the experimental investigation by Dr. SCHEFFER my expectations have proved to be correct, and he has even succeeded in observing the course of the  $p, T$ -line for given value of  $x$  up to a certain distance from the ether side, and found it in perfect harmony with the course predicted by theory for completely miscible substances. He has even succeeded in reaching the value of  $x$  at which the plaitpoint entirely coincides with the critical circumstances for such a mixture taken as homogeneous. According to this experimental investigation, of which I express my sincere admiration, the value of  $x$  at which the minimum value of  $(T_k)_c$  occurs, is so close to the ether side that we may put this value  $=1$ , and the second value mentioned of  $x$  is at a distance of more than 0,3 from the ether side, so that we may put it smaller than 0,7. For smaller value of  $x$  the non-miscibility, as a new circumstance occurring in this system, prevents the observation of the course of the ordinary plaitpoint line.

In my investigation of the causes of imperfect miscibility and of the different forms which can occur for only partial miscibility, I was led to apply a simplification in the theory, which I thought that though certainly of influence on the quantitative accuracy, would be of little or no influence on the qualitative course of the pheno-



mena. In how far this is the case further investigation will have to decide. The simplification consisted in this that for the value of  $b_x$ , which according to the theory is equal to  $b_1(1-x) + 2b_{12}x(1-x) + b_2x^2$ , I assumed the value

$$b_x = b_1 + x(b_2 - b_1).$$

With the simplified form  $b_x$  numerous calculations appeared to be easily feasible which otherwise would lead to too intricate computations.

The simplification of  $b_x$  comes to this that we put  $2b_{12} = b_1 + b_2$ . The theoretical value of  $b_{12}$  can be calculated and leads, whether one starts from the idea that  $b$  is determined by the increase of the number of collisions in consequence of the dimensions of the molecules or by means of the theorem of the virial, to the same result. By both ways one finds  $b_1 = 4$  times the molecular volume of the 1<sup>st</sup> substance, in the same way  $b_2 = 4$  times the molecular volume of the 2<sup>nd</sup> substance, and  $b_{12} = 4$  times the molecular volume of a fictitious substance consisting of molecules the dimensions of which are between those of the two substances. If the molecules could be regarded as spheres the radii of which we take  $= r_1$  and  $r_2$ ,

so that  $b_1 = \sum \frac{1}{2} \frac{4}{3} \pi (r_1)^3$  and  $b_2 = \sum \frac{1}{2} \frac{4}{3} \pi (r_2)^3$ , then

$$b_{12} = \sum \frac{1}{2} \frac{4}{3} \pi \left( \frac{r_1 + r_2}{2} \right)^3. \text{ If we put } b_2 = nb_1, \text{ then } b_{12} = \left( \frac{1 + \sqrt[n]{n}}{2} \right)^3 b_1.$$

The three quantities  $b_1$ ,  $b_2$ , and  $b_{12}$  are therefore determined by the distances of the centres at the collision of the similar and the dissimilar molecules. Hence according to the theory  $b_1 + b_2 - 2b_{12}$  is not equal to 0,

but equal to  $\frac{3}{4} (\sqrt[n]{n} + 1) (\sqrt[n]{n} - 1)^2 b_1$ . We subjoin some values of this

quantity for values of  $n$  between 1 and 3.

$\sqrt[n]{n}$	1,1	1,2	1,3	1,4	1,5	1,6	1,7	1,75	1,8	1,9	2
$n$	1,331	1,728	2,197	2,744	3,375	4,098	4,913	5,36	5,832	6,859	8
$\frac{b_{12}}{b_1}$	1,1576	1,331	1,521	1,728	1,953	2,197	2,44	2,6	2,744	3,048	3,375
$\frac{1+n}{2}$	1,1655	1,364	1,5985	1,872	2,1875	2,598	2,96	3,18	3,416	3,9285	4,5
$\frac{b_1 + b_2 - 2b_{12}}{b_1}$	0,0158	0,064	0,155	0,288	0,469	0,704	1,03	1,18	1,344	1,77	2,25

It is seen from these values that if one puts  $\frac{n+1}{2}$  for  $\frac{b_{12}}{b_1}$  instead of  $\left( \frac{1 + \sqrt[n]{n}}{2} \right)^3$  for a value of  $n$  which is not great, the difference is not much, but that the difference is already considerable for  $n$  greater than 5, to which I concluded for the system ether-water.

For  $n = 5,36$  we have  $\frac{n+1}{2} = 3,18$  and  $\left(\frac{1+13/n}{2}\right)^3 = 2,6$ .

Let us examine what influence this has on the expectation whether minimum  $(T_k)_x$  will occur for a given system or not.

If this occurst hen  $\frac{d\frac{a}{b}}{dx}$  is negative for  $x = 0$  and positive for  $x = 1$ .<sup>1)</sup>  
Hence  $\frac{2(a_{12} - a_1)}{a_1} < \frac{2(b_{12} - b_1)}{b_1}$  for  $x = 0$ . Let us think the value of  $a_x$  given thus:

$$a_x = a_1 + 2(a_{12} - a_1)x + (a_1 + a_2 - 2a_{12})x^2,$$

and  $b_x$  in a similar form:

$$b_x = b_1 + 2(b_{12} - b_1)x + (b_1 + b_2 - 2b_{12})x^2.$$

The quantity  $\frac{d\frac{a}{b}}{dx}$  has the same sign as  $\frac{d\frac{a}{b}}{dx}$ . For  $x = 0$  we have therefore  $\frac{a_{12}}{a_1} < \frac{b_{12}}{b_1}$  or  $\frac{a_{12}}{b_{12}} < \frac{a_1}{b_1}$ . We find for  $x = 1$

$$\frac{2(a_{12} - a_1) + 2(a_1 + a_2 - 2a_{12})}{a_2} > \frac{2(b_{12} - b_1) + 2(b_1 + b_2 - 2b_{12})}{b_2}$$

or

$$\frac{a_2 - a_{12}}{a_2} > \frac{b_2 - b_{12}}{b_2}$$

or

$$\frac{a_{12}}{b_{12}} < \frac{a_2}{b_2}.$$

I concluded already to these relations in my "Théorie moléculaire".  
For the existence of a maximum  $(T_k)_x$   $\frac{a_{12}}{b_{12}}$  would have to be greater than  $\frac{a_1}{b_1}$  and  $\frac{a_2}{b_2}$ .

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1) In this investigation I have assumed that  $RT_{kr} = \frac{8}{27} \frac{a}{b}$ . According to an earlier communication (These Proc. XIII p. 1216) I demonstrated that  $RT_{kr} = \frac{8}{27} \frac{a}{b_g} \frac{8}{rs}$ , and that  $(rs)$  will have to lie somewhat below 8. So if I put  $\frac{dT_k}{T_k dx} = \frac{da}{a dx} - \frac{db_g}{b_g dx}$ , I neglect  $-\frac{d(rs)}{(rs)dx}$ , which may perhaps give rise to an error of importance for widely differing components.

If we write  $a_{12} = l \sqrt{a_1 a_2}$ ,  $\frac{a_{12}}{b_{12}} < \frac{a_1}{b_1}$  leads to the following equation :

$$\frac{l \sqrt{a_1 a_2}}{\sqrt{b_1 b_2}} \frac{\sqrt{b_1 b_2}}{b_{12}} < \frac{a_1}{b_1}$$

or

$$l \frac{\sqrt{\frac{a_2}{b_2}}}{\sqrt{\frac{a_1}{b_1}}} < \frac{b_{12}}{\sqrt{b_1 b_2}}$$

or

$$l \sqrt{\frac{T_{k_2}}{T_{k_1}}} < \frac{(\sqrt[3]{n+1})^3}{8\sqrt{n}}$$

And in the same way  $\frac{a_{12}}{b_{12}} < \frac{a_2}{b_2}$

$$l \frac{\sqrt{a_1 a_2}}{\sqrt{b_1 b_2}} \frac{\sqrt{b_1 b_2}}{b_{12}} < \frac{a_2}{b_2}$$

or

$$l \sqrt{\frac{T_{k_1}}{T_{k_2}}} < \frac{(\sqrt[3]{n+1})^3}{8\sqrt{n}}$$

Now we can put two extreme cases, viz. that  $\frac{a}{b}$  continually decreases till at  $x=1$  the minimum value has just been reached, or that the minimum value begins at  $x=0$  and that the quantity  $\frac{a}{b}$  becomes greater for all successive values.

In the first case, which is entirely, or almost entirely realized for the system water-ether,  $l \sqrt{\frac{T_{k_2}}{T_{k_1}}} < \frac{(\sqrt[3]{n+1})^3}{8\sqrt{n}}$  and

$$l \sqrt{\frac{T_{k_1}}{T_{k_2}}} = \frac{(\sqrt[3]{n+1})^3}{8\sqrt{n}}$$

In the second case

$$l \sqrt{\frac{T_{k_2}}{T_{k_1}}} = \frac{(\sqrt[3]{n+1})^3}{8\sqrt{n}}$$

and

$$l \sqrt{\frac{T_{k_1}}{T_{k_2}}} < \frac{(\sqrt[3]{n+1})^3}{8\sqrt{n}}.$$

In both cases the higher critical temperature is in the numerator in the expression  $\sqrt{\frac{T_{k_1}}{T_{k_2}}}$  or  $\sqrt{\frac{T_{k_2}}{T_{k_1}}}$  where the sign  $=$  occurs and the formula:

$$l \sqrt{\frac{T_{k_2}}{T_{k_1}}} \text{ or } l \sqrt{\frac{T_{k_1}}{T_{k_2}}} = \frac{(\sqrt[3]{n+1})^3}{8\sqrt{n}}$$

may be considered as containing the highest ratio of the critical temperatures of the two components at which minimum critical temperature is still found.

If this ratio is smaller, there is a lowest value of  $T_k$  for certain value of  $x$ . At exactly the ratio given by the formula, this lowest value is either at  $x=0$  or at  $x=1$ . And that in these two cases the ratio of the critical temperatures is the same, is the consequence of a property of  $\frac{(\sqrt[3]{n+1})^3}{8\sqrt{n}}$  to have the same value for  $\frac{1}{n}$  instead of for  $n$ . Only if  $l$  should have a different value, the equality of  $\sqrt{\frac{T_{k_1}}{T_{k_2}}}$  and  $\sqrt{\frac{T_{k_2}}{T_{k_1}}}$  would no longer hold.

Hence it is necessary to calculate  $l \sqrt{\frac{T_{k_1}}{T_{k_2}}}$  or  $l \sqrt{\frac{T_{k_2}}{T_{k_1}}}$  to find  $\frac{b_{12}}{\sqrt{b_1 b_2}}$ . In the above given table, in which the values of  $\frac{b_{12}}{b_1}$  have been given for different value of  $n$ , we must divide  $\frac{b_{12}}{b_1}$  by  $\sqrt[3]{n}$ . And this greatly reduces the value for large value of  $n$ , but it always remains larger than 1. It follows from this that  $b_{12} > \sqrt{b_1 b_2}$ . For small values of  $n$  it is nearly 1. For the above given values of  $\sqrt[3]{n}$ , I have calculated the value of  $\frac{b_{12}}{b}$  and that of  $\sqrt[3]{n}$ , and given it in the following table.

$n$	1,331	1,728	2,197	2,744	3,375	4,098	4,913	5,36	5,832	6,859	8
$\frac{b_{12}}{b_1}$	1,1576	1,331	1,521	1,728	1,953	2,197	2,44	2,6	2,744	3,048	3,375
$\sqrt[3]{n}$	1,1576	1,318	1,482	1,656	1,837	2,023	2,23	2,32	2,41	2,62	2,829
$\frac{b_{12}}{\sqrt{b_1 b_2}}$	1	1,01	1,027	1,044	1,063	1,086	1,094	1,12	1,134	1,17	1,19

Before applying the formula  $l \sqrt{\frac{T_1}{T_2}} = \frac{b_{12}}{\sqrt{b_1 b_2}}$  to the system water ether, I first wanted to examine what value would follow for  $l$  with the values  $a_1$ ,  $a_2$ , and  $n$ , at which I had arrived in a previous investigation. I had concluded to an exceedingly small value for  $\epsilon_2$ , and to a value little below 6 for  $\epsilon_1$ , while I had come to a value lying between 5 and  $5\frac{1}{2}$  for  $n$ .

If we again put  $a_{12} = l\sqrt{a_1 a_2}$  and  $a_1 = 1 + \epsilon_1$  and  $a_2 = n^2(1 + \epsilon_2)$  in  $\frac{a_{12}}{a_2} = \frac{b_{12}}{b_2}$ , we get  $\frac{l\sqrt{a_1 a_2}}{a_2} = \frac{b_{12}}{b_2}$  or  $\frac{l\sqrt{(1 + \epsilon_1)}}{\sqrt{(1 + \epsilon_2)}} = \frac{b_{12}}{b_1}$ .

For  $n = 5,36$  we have  $\frac{b_{12}}{b_1} = 2,6$ , and  $\sqrt{7}$  being  $= 2,65$  we find:

$$l = \frac{2,6}{2,65}$$

which is very near 1 viz. 0.98. With  $b_{12} = \frac{1+n}{2}$  we should have

found  $l = \frac{3,18}{2,65}$ , so about 1,2. And as I have, indeed, repeatedly met

with  $l < 1$ , but never with  $l > 1$ , this is the reason that has induced me to try whether the theoretical value of  $b_{12}$  would harmonize better with the observations than the simplified assumption, which implies that  $b = b_1 \{1 + (n-1)x\}$ . And the result obtained with the theoretical value of  $b_{12}$  even leads us to consider the question for a moment, whether if we could always introduce it,  $l$  would not always appear to be  $= 1$ . But we have first to examine in how far the values of  $\varepsilon_1 \varepsilon_2$  and  $n$  put by me for the ratio of the size of the molecules of water and ether, will appear to be correct. Thus for  $n = 4$  the value of  $\frac{b_{12}}{b_1}$  would be equal to about 2.19 with the same value of  $\varepsilon_1$  and  $\varepsilon_2$ , and hence

$$l 2,65 = 2,19$$

or

$$l = 0,81$$

Now as I recently demonstrated (see among others Arch Néerl. Série III A. Tome 1 p. 136 etc.), we can calculate the value of  $a$  for a substance pretty accurately. We then found :

$$\frac{(RT_k)^2}{p_k} = a \frac{s^2}{f-1}$$

And as for all substances, only with the exception of methyl alcohol, the value of  $\frac{s^2}{f-1} = \frac{64}{27}$ , we have :

$$a = \frac{27 (RT_{cr})^2}{64 p_c}$$

For water with  $RT_{cr} = \frac{638}{273}$  and  $p_{cr} = 190$ , this yields the value of:

$$a_w = 0,01204$$

And for ether with  $RT_{cr} = \frac{467}{273}$  and  $p_{cr} = 35$  the value of :

$$a_{eth} = 0,0353.$$

For  $\frac{a_2}{a_1}$  we find with this 2,932 and  $\sqrt{\frac{a_2}{a_1}} = 1.712$ . Hence  $\frac{a_{12}}{a_2} = \frac{b_{12}}{b_2}$  becomes equal to  $\frac{l}{1.712} = \frac{(1+\sqrt[n]{n})^3}{8n}$ .

That I put  $1 + \varepsilon_1 = 7$  and  $\varepsilon_2$  almost 0 was the consequence of my opinion, which some circumstances had led me to accept, that  $n$  would be about 5, for  $\frac{1+\varepsilon_1}{n^2}$  being  $= \frac{1}{3,513}$ , it follows from  $n = 5$  that

$$1 + \varepsilon_1 = \frac{n^2}{3,513} = \frac{25}{3,513} = 7,1$$

We have, however, not been able to find a formula for the accurate determination of  $b_g$  for a substance. We can, indeed, give the form :

$$b_g = \frac{(RT_{cr})}{\rho_{cr}} \frac{1}{rs}$$

But about  $rs$ , for which 8 is an approximate value, we know only that this product is  $< 8$ , and probably the smaller, as  $b$  is more variable and decreases more rapidly with decrease of  $v$ . If we attribute this change of  $b$  to the compressibility of the molecule,  $rs$  will be the smaller as the molecule is the more compressible.

We then find  $(b_g)_w = \frac{0,0123}{(rs)_w}$  for water and  $(b_g)_e = \frac{0,0488}{(rs)_e}$  for ether.

For  $\frac{b_e}{b_w} = n$  we find  $\frac{0,0488}{0,0123} \frac{(rs)_w}{(rs)_e} = 3,92 \frac{(rs)_w}{(rs)_e}$ . Neither for water nor for ether, however, is the investigation exhaustive enough to enable us to conclude to the value of  $rs$  with perfect certainty. And so we can only assume a value of about 4 for  $n$  with some reservation. That I assumed  $n$  to be a little more than 5 before, was because I only intended then to investigate the behaviour of a binary mixture that should behave in somewhat the same way as the system ether water.

With  $n$  equal to 4,098 we found from  $\frac{l}{1,712} = \frac{2,197}{4,098}$  for  $l$  the value 0,91.

If after this digression we return to the equation

$$l \sqrt{\frac{(T_k)_w}{(T_k)_e}} = \frac{(\sqrt[n]{n}+1)^3}{8\sqrt[n]{n}}$$

we shall have to find the same value for  $l$ , because we have put the value of  $(rs)_w = (rs)_e$  in our former calculations. It appears from everything that from this equation we can calculate the highest value

of  $\frac{(T_k)_1}{(T_k)_2}$  or  $\frac{(T_k)_2}{(T_k)_1}$  at which minimum value of  $(T_k)_x$  can occur with a rather high degree of approximation. But the uncertainty, or rather our ignorance of the value of  $l$  prevents a sharp determination. What precedes is of use at least in so far that it gives the reason why in the first experimental investigation about binary mixtures, for which the value of  $T_k$  differed so little for the two components, minimum  $(T_k)_x$  was of such frequent occurrence.

Let us now proceed to the determination of the value of  $x$  at which the plaitpoint coincides with the critical point for the mixture taken as homogeneous. For this mixture the  $p, T$ -figure is not rounded, but the vapour and the liquid branch touch each other in the plaitpoint; they also touch the  $p, T$ -line of the plaitpoints and the  $p, T$ -line of the critical points. From  $\frac{(RT)^2}{p} = \frac{64}{27} a$  follows:

$$\frac{2dT}{Tdx} - \frac{1}{p} \frac{dp}{dx} = \frac{da}{adx}$$

and with  $\frac{RT}{p} = b(rs)$ , if we neglect the variation of  $(rs)$  follows:

$$\frac{dT}{Tdx} - \frac{1}{p} \frac{dp}{dx} = \frac{db}{bdx}$$

If we put  $\frac{T}{p} \frac{dp}{dT} = f_x$ , we find by division:

$$\frac{\frac{1}{a} \frac{da}{dx}}{\frac{1}{b} \frac{db}{dx}} = \frac{2 - f_x}{1 - f_x} \text{ of } \frac{f_x - 2}{f_x - 1}$$

as I assumed already before but without a rigorous proof, and without demonstrating that on account of the probable variability of  $(rs)$  the relation only holds with a high degree of approximation.

If we have two components for which the value of  $f$  does not differ much,  $f_x$ , which will probably lie between  $f_1$  and  $f_2$ , will not differ much either. For the mixture water-ether  $f_x$  may be put  $\approx 7$  approximately, at least not far from the ether side, hence we must determine  $x$  from the equation:

$$\frac{2(a_{12} - a_1) + 2x(a_1 + a_2 - 2a_{12})}{a_1 + 2(a_{12} - a_1)x + (a_1 + a_2 - 2a_{12})x^2} = \frac{5}{6} \frac{2(b_{12} - b_1) + 2x(b_1 + b_2 - 2b_{12})}{b_1 + 2(b_{12} - b)x + x^2(b_1 + b_2 - 2b_{12})}$$

With  $\frac{a_1}{a_2} = 2,932$  or  $\sqrt{\frac{a_1}{a_2}} = 1,712$  and  $l = 0,91$  and with  $\frac{b_2}{b_1} = 4,098$  this equation becomes:

$$\frac{0,5579 + 0,816 x}{1 + 1,1158 x + 0,816 x^2} = \frac{5}{6} \frac{1,197 + 0,702 x}{1 + 2,394 x + 0,702 x^2}.$$

For  $x = 1$  the first member is equal to 0,468, and the second member  $\left(\text{without the factor } \frac{5}{6}\right)$  equal to 0,464, so almost the same. For  $x = 0$  the first member = 0,5572, and the second member equal to 1,197. To obtain equality the factor would have to be smaller than  $\frac{1}{2}$ . For  $x = 0,6$ , the first member becomes equal to 0,535 and the second member equal to 0,6, so that the factor would be equal to 0,89, which would be slightly too great according to the probable value of  $f_x$ . With  $f_x = 7$ ,  $\frac{f_x - 2}{f_x - 1}$  is equal to 0,83. SCHEFFER'S observations, therefore, yield a value for  $x$  somewhat greater than the value of  $x$  which satisfies the given equation. Possibly the constants occurring in this equation, may have to be revised, and  $n$  put somewhat smaller than 4,098. The value of  $p_c$  for ether, which was found by SCHEFFER larger than 35 (viz. 36,1), would also point in the same direction. But then  $l$  is also reduced to a smaller value than 0,91.

As may be supposed as known, the plaitpoints on the  $p, T$ -lines for constant value of  $x$  do not lie at the highest value of  $T$ . Between the value of  $x$  for the minimum critical temperature and that of the remarkable point they lie on the vapour branch, and in the remarkable point they are transferred to the liquid branch. But for the values of  $x$  which differ little from this point, the distance between vapour branch and liquid branch is very slight, and in the point itself the distance is zero. From the values printed by Dr. SCHEFFER in large type the value of  $\frac{T dp}{p dT}$  for the plaitpoint line in the neighbourhood of the remarkable point can be, therefore, calculated with close approximation. Then, however,  $\frac{T dp}{p dT} = 9,4$  is found even for the highest value of the water-content, and so certainly higher than  $f_x$ . From the course of the three-phase pressure this value is found to be 7,03 at the highest temperature, and this goes to support the expectation that the three-phase line touches the plaitpoint line. But at the same time this shows that the remarkable



point lies at somewhat higher water content than that at which Dr. SCHEFFER has been able to continue his observations.

If the highest point of the three-phase  $pT$ -line is taken as the remarkable point, one finds the value 0,024 for  $a_x$  from  $\frac{(RT)^2}{p} = \frac{64}{27} a_x$ , with  $T = 202,2 + 273$  and  $p = 51,8$ . The value assumed by us for  $a_x$  above, viz.:

$$a_x = a_1 \{1 + 1,1158 x + 0,816 x^2\}$$

or

$$2,022 = 1 + 1,1158 x + 0,816 x^2$$

would yield 0,627 for the value of  $x$ , and hence for  $x$  reckoned from the 2<sup>nd</sup> component, the value 0,373.

But small differences in the data change  $x$  considerably.

So with  $l = 0,9$ , hence also slightly changed value for  $\frac{a_x}{a_1}$  a value of  $x = 0,68$  is calculated, and so  $x = 0,32$  reckoned from the ether-side, which is only slightly higher than the  $x$  to which Dr. SCHEFFER carried up his observations. And that the value of  $x$  for the remarkable point lies higher, appears also from the value of  $\frac{T dp}{p dT}$ , which still has the value 9 instead of 7.

If the ratio of the critical temperatures of the components is below the above given limiting value, then minimum  $T_k$  is found at certain value of  $x$ . As has already been stated only just there where  $\frac{1}{a} \frac{da}{dx} = \frac{1}{b} \frac{db}{dx}$ , when  $(rs)$  has the same value for the two components and for the intermediate mixtures taken as homogeneous. If  $(rs)$  differs, then where  $\frac{da}{adx} = \frac{db}{bdx} + \frac{d(rs)}{(rs)dx}$ . For the mixture for which  $\frac{1}{a} \frac{da}{dx} = \frac{1}{b} \frac{db}{dx}$ ,  $\frac{dT_k}{T_k dx} = -\frac{d(rs)}{rs dx}$ , hence the minimum has slightly been shifted to the component for which  $(rs)$  is smallest. But if we disregard this probably small difference, we can derive the following rule for the place of minimum  $T_k$ . Then:

$$\frac{1}{a} \frac{da}{dx} = \frac{1}{b_x} \frac{db_x}{dx}$$

or

$$\frac{(a_{12} - a_1) + (a_1 + a_2 - 2a_{12})x}{a_1 + 2(a_{12} - a_1)x + (a_1 + a_2 - 2a_{12})x^2} = \frac{(b_{12} - b_1) + (b_1 + b_2 - 2b_{12})x}{b_1 + 2(b_{12} - b_1)x + (b_1 + b_2 - 2b_{12})x^2}$$

If both members are multiplied by  $x$ , and subtracted from 1, we get :

$$\frac{a_1 + (a_{12} - a_1)x}{a_1 + 2(a_{12} - a_1)x + (a_1 + a_2 - 2a_{12})x^2} = \frac{b_1 + (b_{12} - b_1)x}{b_1 + 2(b_{12} - b_1)x + (b_1 + b_2 - 2b_{12})x^2}$$

From the equation derived from this, :

$$\frac{(a_{12} - a_1) + (a_1 + a_2 - 2a_{12})x}{a_1 + (a_{12} - a_1)x} = \frac{(b_{12} - b_1) + (b_1 + b_2 - 2b_{12})x}{b_1 + (b_{12} - b_1)x}$$

or

$$\frac{(a_{12} - a_1)(1 - x) + (a_2 - a_{12})x}{a_1(1 - x) + a_{12}x} = \frac{(b_{12} - b_1)(1 - x) + (b_2 - b_{12})x}{b_1(1 - x) + b_{12}x}$$

or

$$\frac{a_{12}(1 - x) + a_2x}{a_1(1 - x) + a_{12}x} = \frac{b_{12}(1 - x) + b_2x}{b_1(1 - x) + b_{12}x}$$

For the case that  $\frac{a_1}{b_1} = \frac{a_2}{b_2}$  or  $T_{k_1} = T_{k_2}$ , we find  $x = \frac{1}{1 + \sqrt{n}}$  and

$$1 - x = \frac{\sqrt{n}}{1 + \sqrt{n}}$$

Let us put the difference of  $T_1$  and  $T_2$  such that  $x = 1$ , just as for the system water-ether. Let us keep  $T_1$  constant, but let us take  $T_2$  variable. With decrease of  $T_2$  the minimum has got outside the figure, and properly speaking  $(T_k)_{\min}$  no longer exists. With increase of  $T_2$  the minimum enters the figure, and moves towards smaller  $x$ . If  $T_2$  has increased so much that it has become equal

o  $T_1$ ,  $x$  has become equal to  $\frac{1}{1 + \sqrt{n}}$ . If we then keep  $T_2$  constant,

so retaining the value which we had assigned to  $T_1$  at first, and if we now make the critical temperature of the first component decrease,

the minimum lies at still lower value than  $\frac{1}{1 + \sqrt{n}}$ , and when we

make this value decrease to the amount that we had originally assigned to  $T_2$ ,  $x$  has become = 0. So the minimum always lies on

that side where  $T_k$  is lowest, reckoned from  $x = \frac{1}{1 + \sqrt{n}}$ .

If  $\frac{T_1}{T_2}$  is put below the limit for which there still exists minimum  $T_k$ , and if with the same value of  $n$   $T_1 > T_2$  is taken in the first case, and  $T_2 > T_1$  in the other case, the values of  $\frac{x}{1-x}$  are different. There is, however, a simple relation between these values,

viz.  $\left(\frac{x}{1-x}\right)_1 = \frac{1}{n} \left(\frac{1-x}{x}\right)_2$ . We arrive at this relation by writing  $mT_2b_2$  for  $a_2$  and the value  $mT_1b_1$  for  $a_1$  in the equation

$$\frac{a_{12} + a_2 \left(\frac{x}{1-x}\right)_1}{a_1 + a_{12} \left(\frac{x}{1-x}\right)_1} = \frac{b_{12} + b_2 \left(\frac{x}{1-x}\right)_1}{b_1 + b_{12} \left(\frac{x}{1-x}\right)_1}.$$

If then  $T_1$  and  $T_2$  are interchanged, the given equation is verified. Only in the case  $T_1 = T_2$   $\left(\frac{x}{1-x}\right)_1$  and  $\left(\frac{x}{1-x}\right)_2$  are of course equal and the value of this quantity is found equal to  $\frac{1}{\sqrt{n}}$ , as was found above. If  $x_1 = 0$ ,  $x_2 = 1$ .

The two equations, from which the given relation can be derived are in the first case, if we put  $\frac{x_1}{1-x_1} = N_1$ :

$$N_1^2 \frac{mT_2b_{12} - a_{12}}{b_1} + N_1m(T_2 - T_1) + \frac{a_{12} - mT_1b_{12}}{b_2} = 0$$

and in the 2<sup>nd</sup> case:

$$N_2^2 \frac{mT_1b_{12} - a_{12}}{b_1} + N_2m(T_1 - T_2) + \frac{a_{12} - mT_2b_{12}}{b_2} = 0.$$

The second equation multiplied by such a factor that in this too the known term becomes equal to that of the first equation, yields  $N_1N_2 = \frac{1}{n}$ .

The increase of pressure, if the system is entered from the ether side, is, however, not so considerable as has been found by Dr. SCHEFFER.

The quantity  $\frac{\Delta p}{\Delta x}$ , which appeared to be almost constant, had for  $x=0,316$  the value  $\frac{15,45}{0,316} = 48,9$ . It is true that strictly speaking this did not refer to the value of the pressure which we call  $p_{cr}$ . But the difference cannot be great for  $x=0,316$ . From the three-phase pressure which we have calculated, terminating at  $x=0,373$ , the value  $\frac{15,7}{0,373} = 42,1$  would follow for  $\frac{\Delta p}{\Delta x}$ . The quantity  $\frac{\Delta p}{\Delta x}$  for  $p_{cr}$  can, of course, not be constant. For water this pressure is 190, and for greater value of  $x$  (reckoned from the ether side) the quantity

$\frac{\Delta p}{\Delta x}$  must rapidly increase. If minimum  $T_{cr}$  is exactly on the ether

side, then  $\frac{1}{a} \frac{da}{dx} = \frac{1}{b_g} \frac{db_g}{dx}$  and so at first the approximate value of

$\frac{1}{p} \frac{dp}{dx} = -\frac{1}{b_g} \frac{db_g}{dx}$ . But if  $(rs)$  differs appreciably from 8, an appreciable

deviation can also occur in this. We find, namely, for  $p_k$  not exactly

$\frac{1}{27} \frac{a}{b_g^2}$ , but  $p_k = \frac{1}{27} \frac{a}{b_g^2} \frac{64}{(rs)^2}$  and so  $\frac{dp_k}{p_k dx} = \frac{1}{a} \frac{da}{dx} - 2 \frac{db_g}{b_g dx} - 2 \frac{d(rs)}{(rs) dx}$ . As

the relation  $0 = \frac{1}{a} \frac{da}{dx} - \frac{1}{b_g} \frac{db_g}{dx} - \frac{d(rs)}{(rs) dx}$  holds for minimum  $T_k$ , also

$\frac{dp_k}{p_k dx} = -\frac{1}{b_g} \frac{db_g}{dx} - \frac{d(rs)}{(rs) dx}$ . As, however, at present, both for ether and

for water the observations at  $T_{cr}$  are not sufficient to allow us to judge about the variability of  $b$ , it must be considered impossible for the present to decide whether  $(rs)$  differs for these substances,

and if so for which of them  $(rs)$  is greater. The value of  $\frac{dp^x}{p_k dx}$ ,

which seems greater than  $-\frac{1}{b_g} \frac{db_g}{dx}$  would lead us to expect that  $(rs)$

is smaller for water than for ether. If this variability of  $b$  is attributed to the compressibility of the molecule, the water molecule would be more compressible than the ether molecule in spite of its simple structure.

**Physics.** — “*The calculation of the thermodynamic potential of mixtures, when a combination can take place between the components.*” By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

1. In Dr. HOENEN'S Thesis for the Doctorate recently published<sup>1)</sup> the usual method of calculation also followed by me in the Arch. TEYLER<sup>2)</sup> and elsewhere is criticised on p. 2—4, with which criticism I cannot entirely concur.

In the cited paper in TEYLER the problem in question has been treated briefly and not very clearly (in a footnote of a few lines),

1) Theorie der thermodynamische functies van mengsels met reageerende componenten en hare toepassingen in de phasenleer; Nijmegen, L. C. G. MALMBERG, 1912.

2) Théorie générale de l'association de molécules semblables et de la combinaison de molécules différentes; Arch. TEYLER (2) 11, 3me partie, p. 1—97.

so that what has been said there can easily give rise to misunderstanding.

But for this very reason I have afterwards once more fully discussed the matter in the *Chemisch Weekblad*<sup>1)</sup>. This paper, however, seems to have escaped the notice of the writer of the Thesis.

Fortunately he admits (see p. 4) that a correct formula has been used by me, which leads to *correct results*. I should have been quite satisfied with this, if not some objections called for further elucidation so as to remove any doubt of the validity of the method followed by me in imitation of GIBBS, VAN DER WAALS and others.

2. It is clear that we may *always* write [for convenience's sake we consider again the formation of a compound (association) of the *equal* molecules of an associating substance, which compound is decomposed to an extent  $\beta$  — but the considerations would, of course, apply to *any* compound, also of *unequal* components]:

$$\psi_{v_0, \beta_0} = \psi_{V, \beta} - \int_{v_0, \beta_0}^{V, \beta} \left[ \left( \frac{\partial \psi}{\partial v} \right)_{\beta} + \left( \frac{\partial \psi}{\partial \beta} \right)_v \frac{d\beta}{dv} \right] dv, \quad \dots \quad (1)$$

because the free energy  $\psi$  is a function of both  $v$  and  $\beta$  ( $T$  taken constant). The quantities  $v_0$  and  $\beta_0$  refer to an arbitrary condensed gas or liquid state; the quantities  $V$  and  $\beta$  to a *very large* gas volume, where accordingly  $\beta$  approaches 1.

Equation 1 is always valid, for the integration is carried out *along the line of equilibrium*, so that the functions  $\psi$  then always refer to *states of equilibrium*, but then  $\left( \frac{\partial \psi}{\partial \beta} \right)_v$  is always equal to zero in consequence of this equilibrium, and we have simply:

$$\psi_{v_0, \beta_0} = \psi_{V, \beta} - \int_{v_0, \beta_0}^{V, \beta} \left( \frac{\partial \psi}{\partial v} \right)_{\beta} dv \quad \dots \quad (1^a)$$

In this  $\left( \frac{\partial \psi}{\partial v} \right)_{\beta} = -p$ , hence applying VAN DER WAALS'S equation of state, we may write:<sup>2)</sup>

$$\psi_{v_0, \beta_0} = \psi_{V, \beta} + \int_{v_0, \beta_0}^{V, \beta} \left[ \frac{(1+\beta)RT}{v-b} - \frac{a}{v^2} \right] dv, \quad \dots \quad (1^b)$$

<sup>1)</sup> Beschouwingen over eenige fundamentele eigenschappen van den thermodynamischen potentiaal; *Chemisch Weekblad* 1909, N<sup>o</sup>. 51, p. 1—8.

<sup>2)</sup> For convenience's sake we suppose viz. dissociation of *double* molecules to simple ones, in which  $n_1 = -1\beta$ ,  $n_2 = 2\beta$ ,  $\sum n_i = n_1 + n_2 = 1 + \beta$ .

in which the quantity  $\beta$  changes every moment, namely between the limits of integration  $\beta_0$  and  $\beta$ , during the integration (see also p. 5 of the paper in the *Chemisch Weekblad*).

But on account of this variability of  $\beta$  the calculation of (1<sup>b</sup>) is rather laborious, because now also  $\beta$  as a function of  $v$  and  $T$  is to be substituted, and the integration can then give rise to difficulties.<sup>1)</sup>

3. It is therefore of importance to sketch a *second* method of calculation of  $\psi_{v_0, \beta_0}$ , in which the said difficulty is evaded. There is, of course, not the slightest objection to the method discussed just now; against the method that will be given now an objection *may* be raised, though it leads to correct results, as Dr. HOENEN admitted.

We have namely also:

$$\psi_{v_0, \beta_0} = \psi_{V, \beta_0} - \int_{v_0, \beta_0}^{V, \beta_0} \left[ \left( \frac{\partial \psi}{\partial v} \right)_{\beta} + \left( \frac{\partial \psi}{\partial \beta} \right)_v \frac{d\beta}{dv} \right] dv, \quad \dots \quad (2)$$

in which, therefore, in the case of expansion to a very large volume  $V$  the degree of dissociation  $\beta$  is kept constant, viz. equal to that of the condensed mixture  $\beta_0$ , which is in internal equilibrium. Now we do not have  $\left( \frac{\partial \psi}{\partial \beta} \right)_v = 0$  under the integral sign, for during the expansion the internal equilibrium is disturbed, but  $\frac{d\beta}{dv} = 0$ , because  $\beta$  remains constant. Just as above we have also here:

$$\psi_{v_0, \beta_0} = \psi_{V, \beta_0} - \int_{v_0, \beta_0}^{V, \beta_0} \left( \frac{\partial \psi}{\partial v} \right)_{\beta} dv, \quad \dots \quad (2^a)$$

or also,  $\left( \frac{\partial \psi}{\partial v} \right)_{\beta}$  being again  $= -p$ , after substitution of the value for  $p$ :

$$\psi_{v_0, \beta_0} = \psi_{V, \beta_0} + \int_{v_0, \beta_0}^{V, \beta_0} \left[ \frac{(1 + \beta_0) RT}{v - b} - \frac{a}{v^2} \right] dv \quad \dots \quad (2^b)$$

That (1<sup>b</sup>), to which no objections can be raised, and (2<sup>b</sup>) against which an objection *might* be advanced lead to *entirely identical* results, I have demonstrated in the cited paper in the *Ch. W.* (p. 7—8), which furnishes at the same time an *indirect* proof also of the

<sup>1)</sup> For also  $a$  and  $b$  are still functions of  $\beta$ .

validity of (2<sup>b</sup>), and it shows that practically the possible objections to the validity of the second method are unfounded.

4. This objection consists in this that now we do not integrate along the states of equilibrium, and that it is therefore questionable whether it is allowed to substitute the known expression of the mixture  $\beta_0$  as a function of  $v$  and  $T$  for  $\psi_{V,\beta_0}$ .

Dr. HOENEN says: strictly speaking it is not allowed, but after some extension of the definitions of the thermodynamic functions, it is.

I will not argue about this, but will only draw attention to what follows.

In my opinion it is namely not of the least importance in the calculation of the function  $\psi$  for a mixture whether the components happen to be in equilibrium or not. For what would else be the meaning of the statement: In case of equilibrium  $\psi$  must be a *minimum*! How can a function be a minimum when the values *outside* the minimum, where therefore there is no internal equilibrium, are declared invalid?

Nobody has as yet taken any notice of the said objection, neither GIBBS in the calculation of the state of dissociation of  $N_2O_4$ , nor VAN DER WAALS<sup>1)</sup> in his numerous calculations on these subjects, and in my opinion justly.

For we write the value of the function  $\psi$  for an *arbitrary* mixture of the components, even though there should be no internal equilibrium, and *then* determine the *special* values of  $\beta$  for which  $\psi$  becomes minimum, (from  $\left(\frac{\partial\psi}{\partial\beta}\right)_v = 0$ ), by which the required concentration of equilibrium is obtained.

It is namely also possible to regard the mixture fictitiously as non-reacting (this fiction is realized in many cases of retardation and similar ones), and write the expression of  $\psi$  which the mixture *would* have if the components really did not interact. For another value of the ratio of mixing  $\beta$  there is another value of  $\psi$  — and for a definite value of  $\beta$  (independent of the constants of energy and entropy determining the equilibrium)  $\psi$  will have a smallest value. Then there is really equilibrium, and now no change in the condition can set in even after ages.

5. Finally I will just reproduce the calculation of § 7 of the cited paper in the Ch. W. (p. 7—8), in which the identity of the methods, represented by the formulae (1<sup>b</sup>) and (2<sup>b</sup>), is proved.

<sup>1)</sup> Cf also VAN DER WAALS-KÖHNSTAMM, p. 159 et seq.

Let us introduce the function  $\zeta$  (the thermodynamic potential) instead of the function  $\psi$  (the free energy); then we have to calculate:

$$\zeta_{v_0, \beta_0} = \zeta_{V, \beta} + \int_{v_0, \beta_0}^{V, \beta} \frac{(1+\beta) RT}{v} dv - p(V-v_0) \quad \dots \quad (1^c)$$

and

$$\zeta_{v_0, \beta_0} = \zeta_{V, \beta_0} + \int_{v_0, \beta_0}^{V, \beta_0} \frac{(1+\beta_0) RT}{v} dv - p(V-v_0) \quad \dots \quad (2^c)$$

For the simplicity of the calculation of (1<sup>c</sup>), where we have to integrate with variable  $\beta$ , we suppose that also the state  $v_0, \beta_0$  is a gas-state, to which the simple law of BOYLE applies.

$\alpha$ . Calculation of (1<sup>c</sup>). As according to a well-known property:

$$\zeta = n_1 \frac{\partial \zeta}{\partial n_1} + n_2 \frac{\partial \zeta}{\partial n_2},$$

we get:

$$\zeta = (1 - \beta) \mu_1 + 2\beta \mu_2 = \mu_1 + \beta(-\mu_1 + 2\mu_2),$$

with  $\frac{\partial \zeta}{\partial n_1} = \mu_1$  and  $\frac{\partial \zeta}{\partial n_2} = \mu_2$  ( $\mu_1$  and  $\mu_2$  are therefore the *molecular* potentials of the components), and with  $n_1 = 1 - \beta$ ,  $n_2 = 2\beta$ .

Now on account of the equilibrium (in (1<sup>c</sup>) we have namely always states of equilibrium) —  $\mu_1 + 2\mu_2 = 0$ <sup>1)</sup>, hence simply:

$$\zeta = \mu_1,$$

i.e. the *total* potential of the mixture is equal to the molecular potential of the first (the dissociating) component [or also equal to twice the potential of the second component].

For  $\mu_1$  we may now further write at the large gasvolume  $V$ :

$$\mu_1 = C_1 - RT \log V + RT + RT \log(1-\beta),$$

in which  $C_1$  is the known temperature function. Hence we may write for (1<sup>c</sup>):

$$\zeta_{v_0, \beta_0} = \left[ C_1 - RT \log V + RT + RT \log(1-\beta) \right] + RT \int_{v_0, \beta_0}^{V, \beta} \frac{1+\beta}{v} dv - p(V-v_0).$$

Now for perfect gases (this follows from the condition of equilibrium —  $\mu_1 + 2\mu_2 = 0$ ):

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<sup>1)</sup> For  $\frac{\partial \zeta}{\partial \beta} = 0$  is identical with  $\frac{\partial \zeta}{\partial n_1} \frac{dn_1}{d\beta} + \frac{\partial \zeta}{\partial n_2} \frac{dn_2}{d\beta} = 0$ , i. e. with  $\mu_1(-1) + \mu_2(2) = 0$ , or with  $-\mu_1 + 2\mu_2 = 0$ .



$$\frac{\beta^2}{1-\beta} = Kv, \quad \dots \quad (a)$$

hence after logarithmic differentiation :

$$\frac{2-\beta}{\beta(1-\beta)} d\beta = \frac{dv}{v},$$

so that the integral becomes :

$$\int_{v_0, \beta_0}^{V, \beta} \frac{(1+\beta)(2-\beta)}{\beta(1-\beta)} d\beta = \left[ \beta + 2 \log \frac{\beta}{1-\beta} \right]_{v_0, \beta_0}^{V, \beta} = (\beta - \beta_0) + \log \left( \frac{\beta^2}{(1-\beta)^2} \frac{(1-\beta_0)^2}{\beta_0^2} \right).$$

In this according to (a)

$$\frac{\beta^2}{(1-\beta)^2} = \frac{Kv}{1-\beta},$$

hence

$$\int = (\beta - \beta_0) + \log \left( \frac{V}{v_0} \frac{1-\beta_0}{1-\beta} \right),$$

and so finally :

$$\begin{aligned} \xi_{v_0, \beta_0} = & \left[ C_1 - RT \log V + RT + RT \log (1-\beta) \right] + \\ & + \left[ RT (\beta - \beta_0) + RT \log \frac{V}{v_0} + RT \log \frac{1-\beta_0}{1-\beta} \right] - RT (\beta - \beta_0), \end{aligned}$$

because  $pV = (1+\beta)RT$  and  $pv_0 = (1+\beta_0)RT$ .

Hence :

$$\xi_{v_0, \beta_0} (= (\mu_1)_{v_0, \beta_0}) = C_1 - RT \log v_0 + RT + RT \log (1-\beta_0), \quad (1^d)$$

the known expression for  $\xi$  or  $\mu$ , when also  $v_0, \beta_0$  refer to a gaseous state.

If the state  $v_0, \beta_0$  had been a liquid state, the correct expression would have been found too, but in this case the integration would have given rise to great difficulties.

$\beta$ . Calculation of (2<sup>c</sup>). Let us write this equation in the form :

$$\xi_{v_0, \beta_0} = \xi_{V, \beta_0} + \int_{v_0, \beta_0}^{V, \beta_0} \frac{\sum n_1 \cdot RT}{v} dv - (\sum n_1 - (\sum n_1)_0) RT,$$

then for the molecular potential  $\mu_1 = \frac{\partial \xi}{\partial n_1}$  holds :

$$(\mu_1)_{v_0, \beta_0} = (\mu_1)_{V, \beta_0} + \int_{v_0, \beta_0}^{V, \beta_0} \frac{RT}{v} dv - (1-1) RT,$$

because for perfect gases  $\frac{dv}{v} = \frac{\sum n_1 \cdot dv_1}{\sum n_1 \cdot v_1} = \frac{dv_1}{v_1}$  is no longer dependent on the molecular values  $n_1$  etc.

Hence :

$$(\mu_1)_{v_0, \beta_0} = (\mu_1)_{V, \beta_0} + RT \log \frac{V}{v_0},$$

and therefore, if we may again put

$$(\mu_1)_{V, \beta_0} = C_1 - RT \log V + RT + RT \log (1 - \beta_0)$$

for  $(\mu_1)_{V, \beta_0}$ , also when there is no equilibrium at the degree of association  $\beta_0$ , finally :

$\xi_{v_0, \beta_0} = (\mu_1)_{v_0, \beta_0} = C_1 - RT \log v_0 + RT + RT \log (1 - \beta_0)$ , . . . (2<sup>d</sup>) quite identical with (1<sup>d</sup>). [For  $(\mu_1)_{v_0, \beta_0}$  may namely be written  $\xi_{v_0, \beta_0}$ , because  $v_0, \beta_0$  represents a state of equilibrium, and hence  $\xi = \mu_1$  (see above)].

This way, which is much shorter than the preceding, and therefore the prevalent one, leads therefore — in spite of  $(\mu_1)_{V, \beta_0}$  being changed into its value, if the mixture  $\beta_0$  is considered as an *arbitrary* one, i. e. apart from the presence or absence of internal equilibrium between the reacting components — to the perfectly accurate expression, which we have found in (1<sup>d</sup>) by the much more lengthy but perfectly unobjectionable way.

Baarn, Oct. 21, 1912.

**Botany.** — *The Linnæan method of describing anatomical structures.*

*Some remarks concerning the paper of Mrs. Dr. MARIE C. STOPES, entitled: "Petrifactions of the earliest European Angiosperms."*

By J. W. MOLL and H. H. JANSSONIUS.

In our "Mikrographie des Holzes der auf Java vorkommenden Baumarten" we are trying to show that important results in systematic Botany can be obtained by anatomical investigations concerning the wood, if these are conducted with sufficient care. For this purpose descriptions of the anatomical structure are necessary, made with careful observance of the rules given by LINNÉ for describing the external appearance of plants. Of course some additions to these rules and some alterations have been necessary, because anatomical and morphological facts belong to somewhat different orders of things and because the microscopic method presents peculiar difficulties. But in the main it is the Linnæan method we apply.

The results obtained in the two first volumes of our work are from a systematic point of view most satisfactory, which we hope will become still more apparent, when after some years the work will be finished. Families, genera and in many cases even species

are easily recognisable from the anatomical structure of their wood alone.

The method used by us, though extremely simple and well known in its principles, by aiming at a complete survey of the anatomical structures, an analysis leaving no rest, becomes a very laborious task, taxing rather heavily the psychical energy of the student. But a somewhat wide experience in these matters has taught us that only by the help of this method, results really worth while are to be attained in anatomical investigations of every kind.

Thus it is our conviction that the eyes of students in anatomy must be gradually opened to this truth. But we feel very well that this is not a result easily to be obtained. It is a notion widely spread among botanists, that every one having some general anatomical knowledge can, without making use of any special method or form, construct with great facility a good and useful description of anatomical structure. Literature more and less recent abounds with proofs of the truth of what has been said here. Descriptions are to be found everywhere, unripe, incomplete, abounding in repetitions and omissions, referring to many things with which the reader is not in the least concerned, unsteady and supported by lots of necessary and unnecessary drawings.<sup>1)</sup>

We cannot see however that up to this date the example we try to give has procured us many followers. Nevertheless we want some because there are most important problems, only to be solved by the cooperation of many botanists using this same Linnean method of micrography.

Therefore we try to avail ourselves of every opportunity offered, to show the value of our method in obtaining results, vainly aimed at otherwise.

Thus some time ago we studied the wood of *Cytisus Adami* and its two components *C. Laburnum* and *C. purpureus*<sup>2)</sup> and were able to show that the wood of *C. Adami* is that of *Laburnum*, very slightly altered, it is true, but by no means in a direction tending to the structure of the wood of *C. purpureus*. This result could in the main have been anticipated from the splendid work of WINKLER and BAUR on this subject and in so far may not be accounted very interesting. But it was valuable as a testimony for the usefulness of our method, because several other botanists had tried in vain to identify this wood.

1) Alph. De Candolle. La Phytographie végétale.

2) Recueil d. trav. bot. Néerl. Vol. VIII- 1911: 333.

Now again a similar opportunity is offered by the publication, some months ago, of an elaborate paper by Mrs. MARIE C. STOPES, entitled: Petrifications of the earliest European Angiosperms<sup>1</sup>).

In this paper detailed anatomical descriptions are given of 3 specimens of fossil wood belonging to the collections of the British Museum of Natural History. These specimens are from the Lower Greensand, a formation of the Cretaceous Period and are considered by the author as representing the oldest European Angiosperms, known up to this date. For this reason a careful study of the interesting specimens was commenced, and descriptions were made, so far as the condition of the specimens permitted.

By far the best preserved specimen was that called *Aptiana radiata*, gen. et spec. nov. We will only treat of this one.

Reading on p. 90 of the paper the discussion of the affinities of *Aptiana radiata*, the prospect does not indeed seem very hopeful. Mrs. STOPES points out that no branch of modern botany is in a more chaotic condition than that dealing with the anatomy of Angiosperms, which from a taxonomic point of view must certainly be admitted.

She considers that it is entirely premature to attempt any discussion of the possible affinities of this fossil. "In evidence of this "I may mention, that for more than a year I have been showing "this fossil wood to many of the leading botanists of this country, "Europe, and America, and that among the numerous opinions kindly "offered, I have been told it resembled closely nearly every family "ranging from the *Gnetites* on one hand to the *Malvales* on the "other. This is not to be interpreted to mean that the woods of all "these families are alike, and that consequently classification of them "is impossible, but it is due to the comparatively few samples that "any one individual studies and to the great range of variations "between the woods of so-called species of so-called genera."

Mrs. STOPES concludes: "The genera which I was able to examine, "which showed most points of likeness to the fossil, were some "species of *Lonicera*, of *Viburnum*, of *Magnolia* and of *Liriodendron*. "On this however I lay no stress and consider that for the present "more definite statements regarding possible affinities would be purely "theoretical and unprofitable."

We have quite another opinion. After the reading of Mrs. STOPES' paper, it occurred at once to us, that *Aptiana* could very well belong to the family of the *Ternstroemiaceae*. And knowing, that

<sup>1</sup>) Phil. Trans. o. t. Roy. Soc. B. Vol. 203. 1912. Pp. 75—100 and Plates 6—8.

with the help of our method we could hope to obtain certainty in this matter, we proceeded at once to testing our hypothesis.

For this purpose the first thing we needed was a Linnean description of the wood of *Aptiana* in order to compare it with the several summarizing descriptions of the wood of whole families, already published in our "Mikrographie des Holzes". Having done this we found, that our first impression had been correct and that *Aptiana* was no doubt a plant belonging to the family of the *Ternstroemiaceae*, very nearly allied to the genus *Eurya*, if not belonging to it indeed.

In order to give the reader the means of judging for himself, we will now go somewhat more in detail, first giving the Linnean description of *Aptiana*, mentioned above, then a translation of our description of a species of *Eurya*, given in the "Mikrographie des Holzes", and ending with a discussion of the results obtained.

The Linnean description of the wood of *Aptiana* now following was of course abstracted from the paper of Mrs. STOPES. The data thus gathered were arranged in the Linnean fashion, according to a form for the description of secondary xylem, which we always use as a basis of our description<sup>1)</sup>. As far as possible Mrs. STOPES' own words were used and the pages where they are to be found were mentioned. But in some cases, where our interpretation disagreed with that of the writer or where characters were described only to be seen in the drawings or photos, this was of course impossible. These passages were printed in italics and if necessary a footnote explains why it was desirable to alter the writer's statement.

### Micrography of the wood of *Aptiana radiata*,

M. C. STOPES, Phil. Trans. Ser. B vol. 203, p. 75.

A stem or branch thick about 3,5 c.m.

#### Topography.

*Annual rings* structurally recognisable<sup>2)</sup>, the limit of some of the rings a little difficult to determine; thick about 0.6 mm. (p. 85). *The number of vessels and their transverse dimensions, also the cavities of the fibre-tracheids in the inner part of the annual ring*

<sup>1)</sup> This form has been published with many others in: "J. W. MOLL. Handbock der Botanische Micrographie". Groningen. 1907. p. 49.

<sup>2)</sup> On p. 85 is added: "but not clearly marked by any noticeable change in the character of the wood or size of the vessels." By studying Pl. 6 Photo 4 and Pl. 7 Photo 6 we have come to an opposite opinion, to that mentioned in the text.

larger than in the outer; the breadth of medullary rays sometimes smaller in the inner part of the ring. Vessels for the rest uniformly distributed; with a few exceptions isolated and standing separated from each other in the radial rows of fibre-tracheids (Plate 6 Photo 4, Plate 7 Photo 6, Plate 8 Photo 10 and text-fig. 1); in one or two cases 2 vessels standing adjacent in the tangential direction, but such pairs are rare (p. 85) and disturb remarkably little the radial rows of the fibre-tracheids (p. 86). *Fibre-tracheids*: the wood appearing to be entirely composed of fibre-tracheids; arranged with considerable regularity in radial rows (p. 86). *Wood parenchyma* scarce and possibly wanting; several times lying just behind vessels, spanning the distance between the rays (text-fig. 1 and p. 86). *Medullary rays*<sup>1)</sup> in 2 kinds. The most numerous principally 1-seriate, 4 to 10 cells in height and simple (*Einfache Markstrahlen*, Mikrographie I. 59). The other kind 4 cells wide — a few 3 or 2 — a dozen cells in height<sup>2)</sup>, often composite (*Zusammengesetzte Markstrahlen*, Mikrographie I. 59)<sup>3)</sup>, consisting of 3 stories. Between the multiseriate rays innumerable 1-seriate rays (p. 86). The medullary rays running between almost every 2 radial rows of tracheids and vessels (p. 84) and in such a way that nearly every fibre or vessel is in direct contact with them (p. 86, see also p. 90). *The cells of 1-seriate rays*

1) A character, described by Mrs. STOPES (p. 87) as a noticeable feature, is the way of dying out or dwindling down to 1 cell thick in transverse section of the broader rays (Pl. 6 Photo 3 and 4 *dm* and text-fig. 4). The authoress says herself: "while it is very possible that, as both Prof. OLIVER and Dr. SCOTT have suggested "to me, this is due to the rays therein lying somewhat oblique, in a radial sense, "so that any transverse section passes through them, yet it remains an unusual "feature in the truly transverse section of the wood, and gives it the character "shown in text-fig. 4, which separates it from any wood with which I am acquainted." Without doubt the explanation given by Prof. OLIVER and Dr. SCOTT is the right one. In our investigations we have very often met with the same phenomenon, which is represented in a considerable number of our figures, e. g. 16, 24, 34, 38, 40, 41 etc., also in that of *Eurya acuminata*, given below.

2) Plate 6 Photo 5 shows that these rays can be at least 3 times this number of cells in height.

3) The term *zusammengesetzte Markstrahlen* was first used by us in our Mikrographie as cited above. The definition of the term is given there as follows: "aus in senkrechter Richtung übereinander gestellten, regelmässig abwechselnden 1- und mehrschichtigen Teilen zusammengesetzt. Die einschichtigen Teile fast immer aus aufrechten Zellen aufgebaut; stets das oberste und unterste Stockwerk bildend. Die mehrschichtigen Teile fast immer aus liegenden Zellen aufgebaut."

The study of p. 87 of Mrs. STOPES' paper, text-fig. 3 and 5, Plate 6 Photo 5 and Plate 8 Photo 11 will convince the reader, that our description, as given in the text, is correct.

having the same shape as those of the 1-seriate stories of the composite rays (Pl. 6 Photo 5).

### Description of the elements.

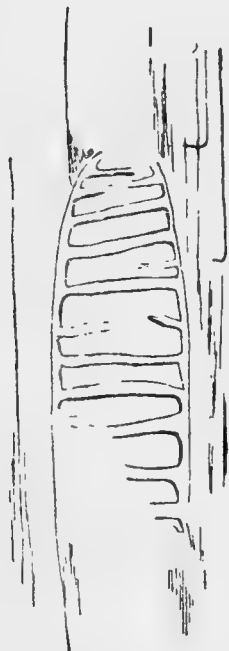


Fig. 1.

*Aptiana radiata*  
Stopes. Transverse wall of vessel; showing scalariform perforation. Reproduction of text-fig. 2 of Mrs. STOPES' paper.

I. *Vessels*. R. and T. 28 to 40  $\mu$ , about 33  $\mu$  being the commonest size. Roughly circular cylinders. *Transverse walls placed very obliquely; with scalariform perforations and horizontal rungs, see fig. 1*<sup>1)</sup>. *Walls thickened, but not remarkably so and the lignified wall much thinner than that of the adjacent cells (fibre-tracheids); — with irregularly placed simple round or slightly oval pits (p. 86).*

II. *Fibre-tracheids* R. and T. 15 to 50 (?)  $\mu$ , the radial dimension often somewhat smaller than the tangential; 4- to 6-, generally 6-angular. *Walls in most cases thickened, the lumen of the cells  $\frac{1}{3}$  or less that of its whole diameter (see Pl. 8 Photo 10 and text-fig. 1); — with bordered pits, on the tangential walls at least as numerous as on the radial (p. 86, Pl. 8 Photo 10, and text-fig. 1); arranged in 1 and in a few cases in 2 slightly irregular rows, not very closely arranged in vertical position, each being spaced at a distance from its neighbour roughly equal to its own diameter; borders of pit-chambers circular (p. 86).*

III. *Wood parenchyma*. *Cells on a transverse section somewhat elongated in the direction of the circumference of the vessels. (Pl. 8 Photo 10 and text-fig. 1). Walls thickened; — with only simple pits. Contents more blackened than that of other cells (p. 86).*

IV. *Cells of medullary rays*. *Walls thickened; pitted (see Pl. 8 Photo 10 m, and p. 89).*

Having completed this description we compared it with the general descriptions of the wood-anatomy of the several families, published in the two first volumes of our "Mikrographie des Holzes". It was soon found that the only family with which the characters of *Aptiana* coincided and did so in a very satisfactory manner, was indeed that of the *Ternstroemiaceae*.

<sup>1)</sup> On p. 86 Mrs. STOPES says: "In longitudinal section not many of the vessels show the character of their walls, but those that do, have broad, simple scalariform pitting (see text-fig. 2)". If a regular Linnean description had been made, this mistake would no doubt have been avoided.

We now sought in this family among the species of which a full description was given, for that which corresponded in the largest number of most essential characters with *Aptiana*. We found that this was the case with *Eurya acuminata* and we reproduce here a literal translation of this description, as given in our *Mikrographie*, but somewhat shortened for the reader's convenience, by omitting all those characters of which no mention is made in the description of *Aptiana*.

If the reader will compare the two descriptions with each other, he can judge for himself of the validity of *Aptiana's* claim to be considered as a member of the family of the *Ternstroemiaceae*.

Micrography of the wood of *Eurya acuminata*,  
DC. Mém. Ternstr. 26.

A stem or branch of about 7 cm.

Topography. (See fig. 2).

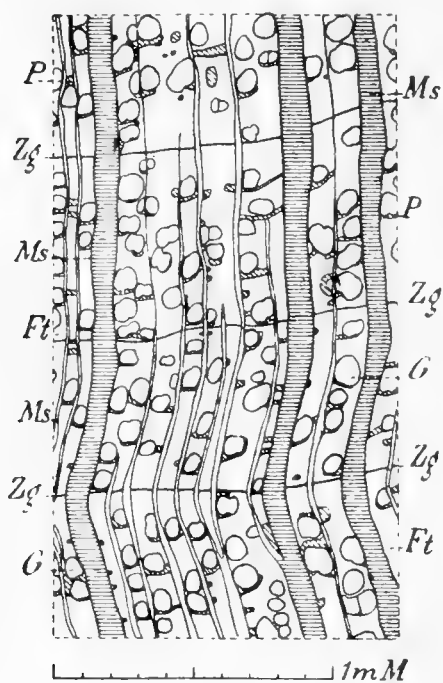


Fig. 2.

*Eurya acuminata*. Transverse section. Zg Annual rings; G Vessels; Ft Fibre-tracheids; P Wood parenchyma; Ms Medullary rays.

Annual rings, especially in the sample most minutely examined, fairly distinct; 0.35 mm to 2.5 mm thick. In several rings a period in the number of vessels and the transverse diameters of vessels, fibre-tracheids and wood parenchyma cells, in the 2 last named elements especially of the radial diameter; the maximum of this period about in the middle of the ring, the minimum in the outer lower than in the inner part, especially for the radial diameter of the fibre-tracheids. The limits of the rings sometimes more distinct, by the number of vessels in the different rings being unequal. On the limits of the rings the medullary rays mostly somewhat broader. Vessels for the rest regularly distributed; almost always isolated, only very seldom in pairs. Fibre-tracheids constituting the groundmass of the wood; only now and then in radial rows. Wood parenchyma scarce, scattered between the fibre-tracheids; when bordering on vessels, on the inner side of these only. Medullary rays in 2 kinds. The most numerous generally 1-, in the middle sometimes 2-seriate, 6 to 30, mostly 10 to 15 cells in height and



simple. The second kind 3- to 6-seriate, up to 150 cells in height, often composite and consisting of 3 stories. The absolute height of the first kind of medullary rays smaller than that of the latter. Between 2 multiseriate medullary rays mostly some 1-seriate. The medullary rays laterally separated by 1 to 4 rows of fibre-tracheids often adjoining vessels. The cells of the 1-seriate rays resembling those of the 1-seriate stories.

*Description of the elements.*

I. *Vessels*. R. 25 to 80  $\mu$ , T. 20 to 70  $\mu$ . Elliptical and circular cylinders or multilateral prisms with rounded edges. Transverse walls placed very obliquely, showing scalariform perforations with 50 to 125 horizontal rungs. The scalariformly perforated part of the transverse walls sometimes 500  $\mu$  in length. *Walls* 1.5  $\mu$  thick; — with numerous transversely elongated bordered pits, when adjoining each other; — with very numerous elongated bordered pits, when adjoining fibre-tracheids; — with a few simple and numerous elongated one-sided bordered pits, when adjoining wood parenchyma cells and upright ray-cells; — with unilateral bordered pits, when adjoining procumbent ray-cells.

II. *Fibre-tracheids*. R. 20 to 30  $\mu$ , T. 25 to 35  $\mu$ ; 4- to 8-angular. *Walls* thick 6 to 8  $\mu$ ; — with numerous elongated bordered pits, when adjoining vessels or each other; these pits more numerous on the tangential than on the radial walls; borders of pit-chambers circular or somewhat elongated in a vertical direction, e.g. 5 by 6  $\mu$ .

III. *Wood parenchyma cells*. Those adjoining vessels mostly elongated in the direction of the circumference of the vessels. *Walls* thick 1.5  $\mu$ ; — with a few simple, and numerous elongated 1-lateral bordered pits, when adjoining vessels; with elongated 1-lateral bordered pits, when adjoining fibre tracheids; — with simple pits when adjoining each other or ray cells. *Contents*: sometimes a few starch grains and some red brown mass on the transverse walls.

IV. *Cells of medullary rays*. Walls thick 1.5  $\mu$  or more; pits the same as in the wood parenchyma cells.

A simple comparison shows, that there is a coincidence in almost every particular, such as cannot be the outcome of accidental circumstances and as in classifying systematic botany must needs lead to identification. As leading features in this comparison we consider the very oblique transverse walls of the vessels, with their scalariform perforations; the groundmass of the wood consisting of fibre tracheids; the excessive scarcity of woodparenchyma and the oc-

currence of composite medullary rays — all of which are characters not found in many families and coinciding only in that of the *Ternstroemiaceae*, *Staphyleaceae* and in some of the *Olacineae*. But the two last could be excluded by differences in several other characters. The objection might perhaps be made, that in our "Mikrographie des Holzes" we have studied only a comparatively small number of families, viz. 33, up to this date, and that it would by no means be impossible, that afterwards another family might be found coinciding as well or even better than that of the *Ternstroemiaceae* with the characters found in *Aptiana*. But we are going right through the system, following the Genera Plantarum of BENTHAM and HOOKER. Thus this objection implies the probability, that in a region of the system far distant from the *Ternstroemiaceae* a family will be found showing an anatomical structure of the wood coinciding in almost every particular with that of the *Ternstroemiaceae*. Our experience in wood matters leads us to tax this probability as infinitely small. But we do not know what lengths some botanists might go in such a matter. The argumentation stated above thus led us to the scientific conviction that *Aptiana* belongs to the *Ternstroemiaceae*.

Having reached this point, we tried, making use of the analytical key for the identification of the species in our Mikrographie and comparing the descriptions of the species whether some nearer ally of *Aptiana* than *Eurya acuminata* could be found. If the reader does the same, he will be led to *Eurya japonica* and *E. glabra*. Therefore we think that the genus *Eurya* may safely be considered as a most near ally of *Aptiana*, leaving it undecided whether both could be united with each other in the genus *Eurya*, which however to us does not seem improbable.

In conclusion we want to say some words on the work of Mrs. STOPES and on the character of the observations made by us. In the foreground must be placed the fact that for the whole of our knowledge of *Aptiana* we are indebted to the careful work of Mrs. STOPES. But we can go farther and trust, that the reader will not have mistaken our work for a criticism of Mrs. STOPES' paper. If we had not indeed considered this paper as a very fair specimen of what at this time may be called good anatomical work, we could not have written as we have done. That bad work does not produce good results is a truth, which we by no means want to prove. We do not criticize a special paper, but the method or rather the want of method still prevailing in almost all anatomical work published at this day. And we think that we have shown how a research on a

very interesting subject, bringing to light a most interesting palae-ontological result and ably conducted, might have brought us still nearer to the truth if the Linnean method had been used in making the descriptions.

This method indeed asks much of the investigator's time and energy and the use of it can only be learnt by patient study. But we mean to say, that at some future time a botanist of Mrs. STOPES' power will not be satisfied with descriptions of anatomical structures made without the use of the Linnean principles of micrography.

*Groningen, Oct. 21<sup>th</sup> 1912.*

**Bacteriology.** — “*On the reaction velocity of Micro-organisms*”.

By Prof. C. EIJKMAN.


(Communicated in the meeting of September 28, 1912).

### I. *Velocity of disinfection.*

Micro-organisms have been the object of various researches as regards the velocity of their reaction, when exposed to external agents. From the experimental evidence brought forward it appeared, that considerable differences exist between individuals of the same species, of the same stock, nay of the same culture: they do not react all about at the same time, but the reaction proceeds in an orderly manner:

It is especially the orderly progress of disinfection of bacteria, under the influence of germicidal agents, either chemical or thermal, which, in virtue of its vital importance for theory as well as for practice, has recently been studied by several investigators.

Attempts have even been made to find a mathematical formula for this gradual process. As I stated before<sup>1)</sup> MADSEN and NYMAN arrived at the conclusion<sup>2)</sup> that in the disinfection of anthrax spores the reaction proceeds according to the equation for the so-called “unimolecular reactions”. This view found favour with most experimenters.

When the reaction is illustrated graphically by plotting the results (abscissae representing the times and ordinates the numbers of survivors), a “curve of survivors” is obtained, having the shape of . This

<sup>1)</sup> Proceedings of the Meeting of 27 Feb. 1909.

<sup>2)</sup> Z. f. Hyg. u. Inf. Kr. Bd. 57, 1907.

being an exponential curve, will become a straight line inclining to the abscissae, if we take the logarithms of the numbers of survivors instead of the numbers themselves.

By expressing the results of the experiments logarithmically, we can see at a glance whether, and how far, they are in accordance with the formula, or whether they depart from it; the absolute values being immaterial in this case, I used for my calculations BRIGG'S logarithms in place of natural logarithms. (cf. H. CHICK).

In order to account for their results MADSEN and NYMAN regard anthrax spores as an aggregation of individuals of differing resistance. If however this dissimilarity were decisive, a totally different type of "curve of survivors" could be expected, as I demonstrated in the *Biochem. Zeitschrift* (Bnd, 11. 1908). Conformably to the frequency-curve of QUÉTELET-GALTON an accumulation of deaths could then be expected at an average moment of the process, the rest of the spores with a lower or higher resistance, dying before or after it in gradually lessening numbers. Consequently the curve of survivors would necessarily assume the  $\curvearrowright$ -form or, when represented logarithmically, the  $\curvearrowleft$ -form and not the shape of  $\searrow$ . (see also fig. 6, page 637).

Experiments with bacillus coli, published by me in a previous paper really brought forward a curve very much like it, which however differed from the one expected in not being symmetrical, as the first half of the germs were killed in much shorter time than the second.

In the case of anthrax spores I obtained since that time results in fair accordance with MADSEN and NYMAN'S experience, just as H. CHICK <sup>1)</sup>, REICHENBACH <sup>2)</sup> and others did.

#### a. Experiments with anthrax spores.

Fig. 1 shows the results of three experiments on disinfection at 80°, 84° and 90°, expressed logarithmically. Their accordance with the formula may be called very satisfactory. The deviations from the straight lines, inclining to the abscissae, are indeed slight. An exception is noticed only at the beginning of the experiment at 80°, where there is hardly a fall in the number of bacteria during the first few minutes. The same had occurred very regularly in my previous experiments with *Bacillus coli*. This period of lag I then took to be an incubation. I learned since, that an analogous

<sup>1)</sup> The Journal of Hygiene, Vol. VIII 1908, Vol. X, 1910.

<sup>2)</sup> Z. f. Hyg. u. Inf. Kr. Bnd. 60, 1911.

phenomenon is observed in purely chemical reactions, and is called "induction" <sup>1)</sup>.

For my experiments I used again suspensions of spores. Of every sample, selected at definite intervals of time, 4—5 parallel cultures were plated, of which I took the average. If the numbers did not mutually agree the experiment was considered to have failed.

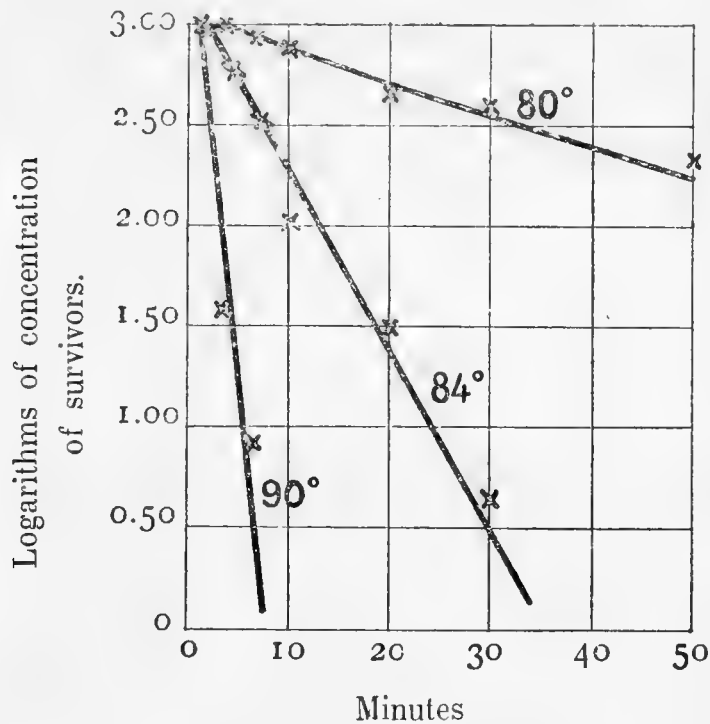


Fig. 1. Disinfection of anthrax spores by heat.

TABLE I. Anthrax spores at 80°.

Time (min.)	Numbers on plates					Mean	Dilution	Number per cc.	Starting number =1000	$\log_{10}$
	1	2	3	4	5					
1	440	422	456	454	454	445	11	4895	1000	3.000
3	431	435	408	454	448	435	11	4785	977	2.990
6	366	343	365	386	406	373	11	4103	838	2.923
10	597	604	605	614	613	607	6	3642	744	2.872
20	724	756	665	729	788	732	3	2196	449	2.652
30	935	950	937	946	921	938	2	1876	383	2.583
50	1159	1081	1077	1022	1024	1073	1	1073	219	2.340

<sup>1)</sup> BUNSEN and ROSCOE, Pogg. Ann. Bnd. 96, 1855.

For an easy survey and comparison of results I started in my graphical illustration from 1000 living bacteria, the numbers obtained by the experiment underwent a corresponding reduction.

Table I contains the numerical data resulting from an experiment.

As I stated before, MADSEN and NYMAN's interpretation of the conformity in the process of unimolecular reactions and the disinfection of anthrax spores is open to doubt. With greater consistency H. CHICK avers not only that the two processes agree outwardly but are even completely analogous :

“The fact that the individuals do not die all at once but at a “rate proportional to the concentration of the survivors at a given “moment, is to be attributed to temporal and rhythmical changes “in resistance, which by an analogy with chemical processes, may “be supposed to be due to temporary energy changes of the constituent proteins.”

Thus putting bacteria on a level with molecules has raised some objections. REICHEL<sup>1)</sup> remarks that this is admissible only if the chances of the germs being attacked by the active mass of the disinfectant were not the same for all bacteria, which in an homogeneous liquid is possible only for particles commensurable as to number and size, such as molecules, not however for micro-organisms and molecules. REICHENBACH thinks so too. He can hardly imagine, that considering the vast difference in size, not all bacteria should be under the same circumstances, relative to the molecules of the germicide. Still less can it be maintained that the bacteria must reach the thermal deathpoint in succession. Moreover considering, that the type of the curve of survivors is not at all determined by the character of the noxious agent, REICHENBACH is induced to think, that the cause is to be looked for only in the micro-organisms themselves, i.e. that differing resistance decides the order of their destruction. The same observer adduces theoretical and experimental evidence to prove, that resistance depends chiefly on the “age” of a generation and shows, by a mathematical treatment, that a culture, having been developed in a definite manner, may contain generations, which, when classified according to their ages form a geometrical series. Assuming moreover that the individual resistance of the cells increases with the age of the generation, this would afford solid ground to account for the orderly progress of disinfection.

It seems to me that this attempt to settle the question is somewhat artificial, its weak point being that REICHENBACH, on the basis

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<sup>1)</sup> Biochem. Z. Bnd. 11, 1908.

of his supposition, shows only how a geometrical series *can* come forth, not however why it always *must* do so, for example in the case of anthrax spores, in spite of varying conditions of growth. This points to a regularity as to the age-distribution, which of itself requires an explanation. In my opinion, the one put forward by REICHENBACH is inadequate.

It would seem then that, if we have to find an explanation, the only way would be to consider the progress of disinfection to be mainly a physico-chemical phenomenon. MADSEN and NYMAN and CHICK lend further support to this view by agreeing that VAN 'T HOFF'S temperature coefficient appears to be applicable in this case.

It may indeed be called in question, whether this material allows of a mathematical treatment, since it can hardly be worked with without committing serious experimental errors. Consequently, as I pointed out in my first paper, the experimental data of the researchers just mentioned, were far from accurate. Their results however, having been corroborated by several other observers, their opinion that the process of disinfection exhibits some analogy to a unimolecular reaction, can no longer be disputed. Setting aside experimental errors, divergencies from the regular process should then be ascribed to individual differences in resistance.

#### b. *Bacillus coli*.

It seems that the individual differences mentioned above are more frequently displayed by vegetative forms than by spores, anyhow they show many more departures from the regular process.

H. CHICK found no less than three types of the curve of survivors for the disinfection of *staphylococcus pyogenes aureus* with hot water. I also refer to Figs. 2 and 3, giving the logarithmic curves for the disinfection of *bac. coli* respectively by heat and with 0,5% phenol. It will be seen from Fig. 2 how three *coli*-cultures *A*, *B* and *C*, though taken from the same stock, when killed by heat, yield very different types. *B* is the only one that corresponds with the type of the unimolecular reaction. *C* shows a marked departure, *A* only a slight one in the opposite direction.

In order to give an idea of the degree of accuracy of this kind of investigations I once more subjoin all the quantitative results of an experiment in Table II. We know that plate-culture is not a very precise quantitative method. Sets of parallel cultures not seldom yield essential differences, even though the sampling may have been

performed with the greatest caution. Our results however, as may

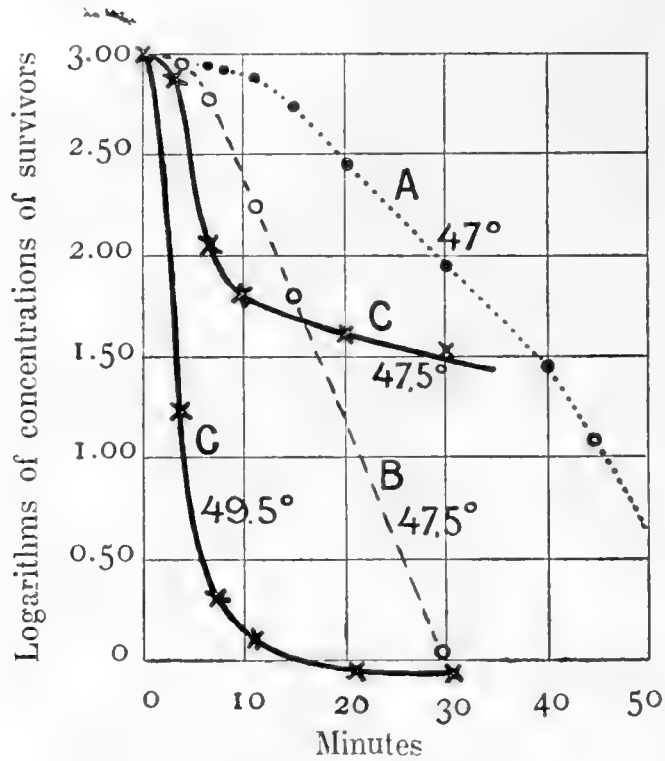


Fig. 2. Disinfection of *Bac. coli*.  
A, B, and C are different cultures.

be roughly concluded from the table are most likely not more inaccurate than those of other investigators on this subject.

TABLE II. Disinfection of *B. coli* (culture C) by heat at 47.5°.

$t$ (Min.)	Numbers on plates				Mean	Starting number = 1000	$\log_{10}$
	1	2	3	4			
1	2016	2086	2100	2035	2059	1000	3.000
3	1547	1495	1558	1498	1525	740	2.869
6	211	270	221	288	248	120	2.079
10	102	129	137	132	125	61	1.785
20	72	76	65	74	72	35	1.544
30	66	80	65	65	69	33.5	1.525

Disinfection of *B. coli* with phenol also yielded types of loga-



Logarithms of concentration of survivors

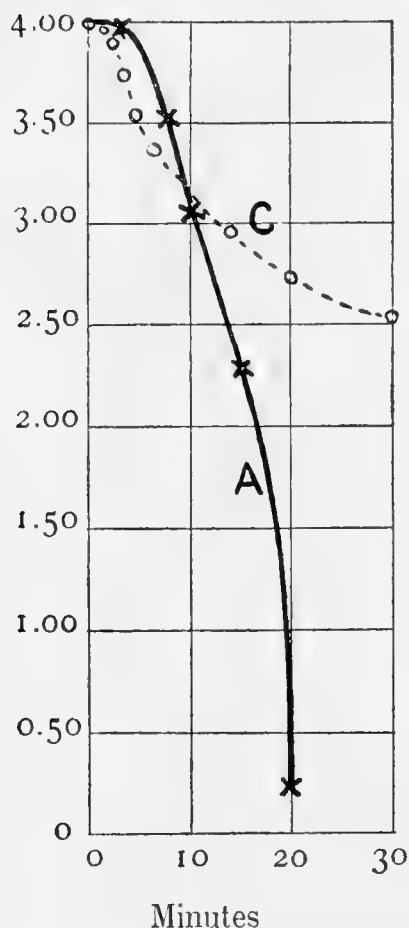


Fig. 3. Coliculture A } 0.5 %  
 „ B } phenol  
 at 22°

rithmic curves of survivors that differed for various cultures. (Fig. 3.).

Both divert from the straight line, so the reaction- or disinfection velocity is not constant: that of *A* increases in the progress of the process, whereas that of *C* diminishes<sup>1)</sup>. The same types were also observed by H. CHICK in the case of vegetative organisms.

Type *C* was also found by REICHENBACH (cf. tab. XIV—XVI l.c.), who worked with very young paratyphus cultures that were killed off by heat at 47—49°. When the culture was older than 13 hours, the exponential curve became smoother, once however it assumed the shape of type *A*.

REICHENBACH attributes the tendency to depart from the straight line in very young cultures to the relatively large number of low-resistant individuals present. It is remarkable, that H. CHICK's experience is just the reverse: the value of *k* diminishes in the course of the process for the older cultures, whereas for the younger ones *k* is smaller and approximately constant.

As for my own experiments (with *Bacillus coli*), for the sake of uniformity in my material I invariably worked with very young cultures and found, as shown in Figs. 2 and 3 departures in either way. Added to the contradictory results of the observers mentioned above, this seems to suggest that the age of the culture does not determine the form of the curve of survivors.

### c. Yeast cells.

It being possible that large cells might lead to other results than small ones, I also made some experiments with yeast cells.

There is perhaps some reason to suppose that speaking generally, in disinfection experiments, whether with thermal or chemical agents, the individuals are destroyed, because the cells, suspended in the liquid, are attacked by molecules, whose caloric velocity exceeds

<sup>1)</sup> The cultures referred to in Fig. 3 and Fig. 2 are not identical, though from the same stock.

a certain limit. A slow process would induce us to think, that these active molecules with a caloric velocity far beyond the average, are only small in number, all the rest being comparatively indifferent. The micro-organisms are then as it were exposed to a continuous shower of bullets (the active molecules) and if this shower be not too dense they will be destroyed in succession and in obedience to the mass-law. Thus the analogy with the unimolecular reaction would be rendered intelligible.

Now, just as in a shower of bullets, the number of "hits" in our case depends on the size of the targets, the larger the individuals are, the more regularly the hits will be distributed among them. We were therefore justified in supposing that, whereas the smaller organisms behave in analogy to the unimolecular reaction, the individual differences of resistance existing among the larger ones become more prominent and express themselves in the form of the curve of survivors.

I do not mean to attach great importance to this illustration, nor to offer its validity as a point to be discussed. I only wanted to set forth why I extended my experiments to larger organisms also.

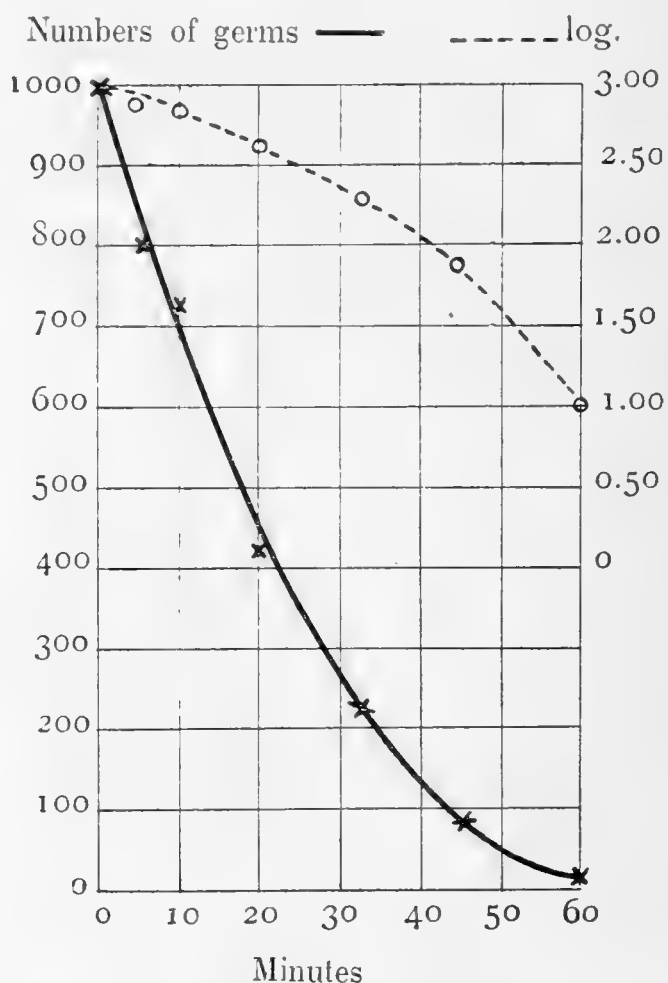
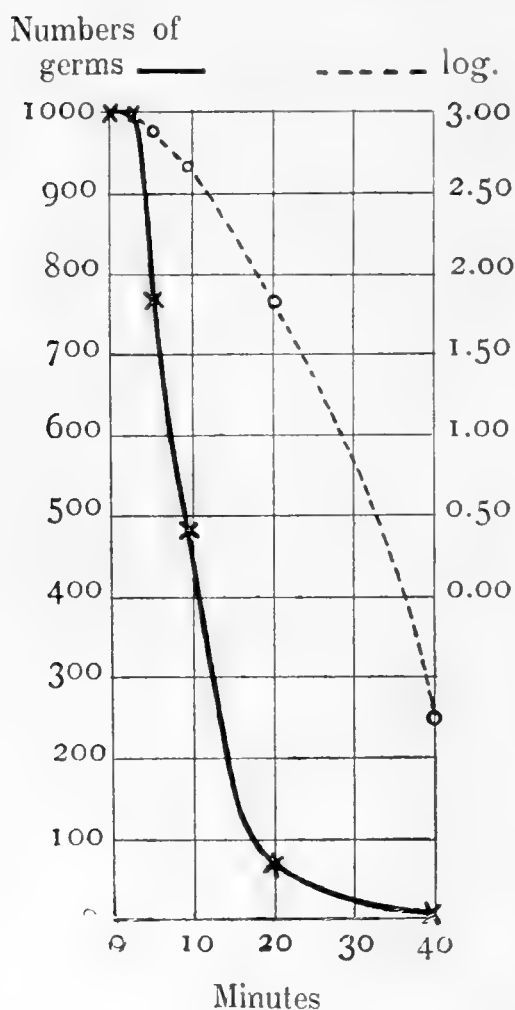


Fig. 4. Rose yeast killed at 47°. . . Fig. 5. Rose yeast with 0.6% Phenol at 25°.

First of all experiments were made with *Blastomyces rosea*, a fairly uniform material, consisting of well isolated cells; their size exceeds that of anthrax spores 90 times in volume and twenty times in surface. The curve of survivors corresponds with type A of *Bacillus coli*, i. e. the value of  $k$  increases continuously during the experiment (Figs. 4 and 5).

The same type appeared invariably also in working with a pure culture of press-yeast.

Numbers of germs ——— ————log.

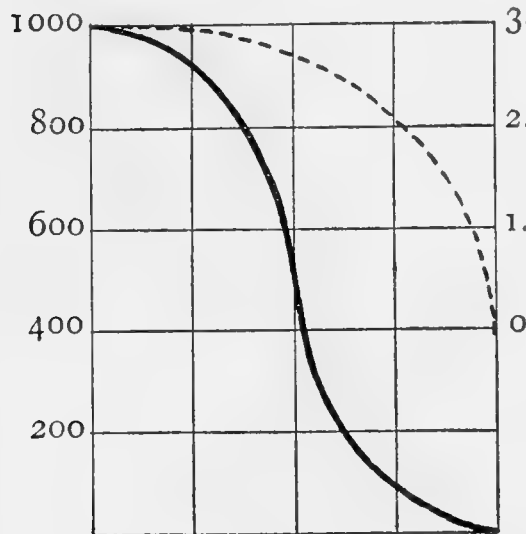


Fig. 6.

Suppose the structure of the cultures according to various degrees of resistance had in this case determined the shape of the curve of survivors, it would not accord entirely with the law of fluctuating variability (QUÉTELET-GALTON). If it did, the curves would look like those in Fig. 6. Intermediate between these and the types of the unimolecular reaction are the curves found for yeast cells.

#### d. Small and large spores.

REICHENBACH published experiments with the spores of a small saprophytic bacillus. The results differed from those with anthrax spores. The order of dying was not in accordance with the formula for the unimolecular reaction, whether disinfection had taken place by heat or with sublimate. During the process the value of  $k$  increased progressively.

As a specimen of small spores I selected those of *Bacillus subtilis*; in all my experiments the results obtained evinced a fair accordance with the formula of the unimolecular reactions. Only towards the end of the reaction  $k$  was always inclined to decrease slightly. This peculiarity is indeed also noticeable in my experiments with anthrax spores (cf. Fig. 1). It is much more conspicuous with large spores (see Fig. 8 and Table III). Here we had to do with spores of a particularly big bacillus obtained by chance from the dust settled in a room. Their dimensions are about twice as long as those of anthrax spores. Four experiments, in which the spores were disinfected by

heat showed invariably that there was at a given moment a rather great fall in the disinfection velocity (Fig. 8).

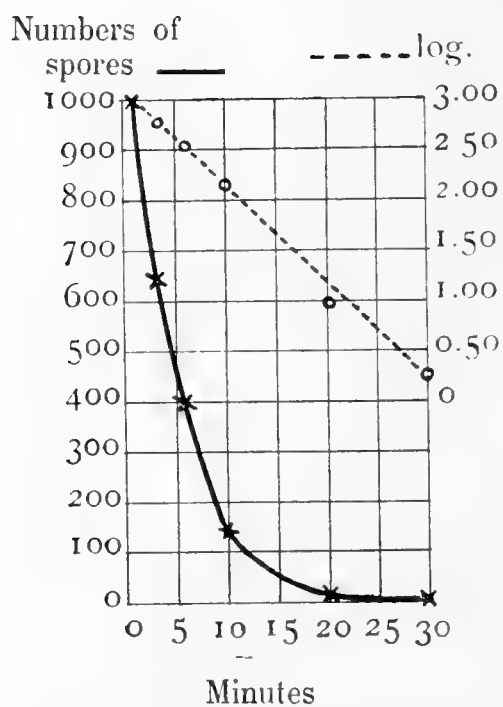


Fig. 7. Small spores at 90°.

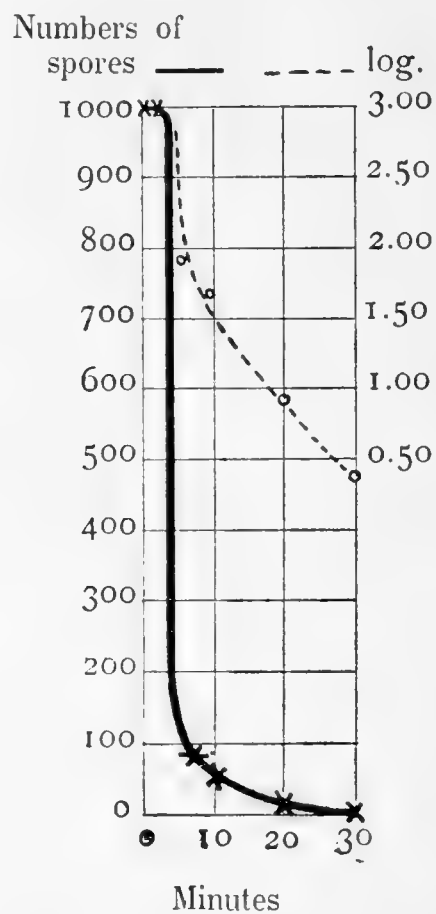


Fig. 8. Large spores at 90°.

This result clashes with the reasoning on page 635, which rather implied a gradual rise in the value of  $k$ , just as with yeast cells.

TABLE III. Large spores at 90°.

Time (min.)	Numbers on plates					Mean	Dilution	Number per cc.	Starting number =1000	$\log_{10}$
	1	2	3	4	5					
1	940	843	826	830	826	853	75	63975	1000	3.000
3	2610	2624	2600	2603	2571	2602	25	65050		
6	420	—	501	431	487	460	11	5060	78.5	1.895
10	520	481	492	441	481	483	6	2898	45	1.653
20	586	530	593	554	438	540	1	540	8.4	0.924
30	163	151	157	146	112	146	1	146	2.3	0.362

II. *Velocity of germination.*

Germination of spores is to be looked upon as a reaction to the favourable conditions of the nutrient medium. As will appear later on, this reaction can be very rapid at the beginning and is very sensitive either way: in a negative as well as in a positive sense. For when favourable and inhibitory influences coincide, the spores are not to be decoyed from their tents: they do not develop. It seems probable therefore that they permanently keep in touch with their medium, from which they are not isolated by their membrane as completely as is commonly admitted.

According to KOCH and others, who watched the process under the microscope, spores take rather a long time (one or more hours) to germinate. Still in this respect individuals differ greatly. When examining the suspended drop, we shall see after some time besides fully developed spores, others still in their original state, and, between these two extremes, others again in various stages of germination.

We alluded to the possibility of indications of growth being given at the very outset. WEIL<sup>1)</sup>, among others, discovered that after 10 minutes' sojourn in broth at 37°, out of 8600 anthrax spores only 60 remained resistant, when heated up to 80° for a short time. This rather surprised him, as he deemed it not likely that the greater portion of the spores should have germinated so rapidly and hence should have become vulnerable at a temperature of 80°. Yet, as also FISCHOEDER<sup>2)</sup> remarks, this is the best way to account for WEIL'S experience, which seems to prove that germination can begin very soon, when the circumstances are favourable. Similarly FISCHOEDER found in his microscopic observation of some spores, already after 5—10 minutes, such alterations in their appearance and in their behaviour towards colouring matter as pointed to germination in an initial stage.

The large spores worked with in my experiments on disinfection, published in this paper, were also now selected for my material. Their very size enables us to perfectly control the process of germination. Their growth optimum is 37° C.

The results I obtained, fully confirmed the observations of WEIL and FISCHOEDER. I agree with the latter, that the decrease of resistance towards heat after a short incubation in broth or serum at a favourable

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<sup>1)</sup> Arch. f. Hyg. Bnd. 39, 1901.

<sup>2)</sup> C. f. Bakt. I. Bnd. 51, 1909.

temperature, is to be considered as the initial indication of a germinating process, not only on the basis of microscopic observation, but also because of the fact, that there is no decrease, when germination is arrested, for instance by adding to the broth  $\frac{1}{2}$  % phenol, or by raising its temperature to  $50^{\circ}$ .

WEIL's and FISCHÖEDER's numerical data do not practically point to an orderly progress of the germination, which was indeed evidenced by our experiments.

Fig. 9, where logarithms of numbers are plotted against time, illustrates graphically the decrease of the thermostable spores in broth. The logarithmic curves, represented by straight lines, prove that germination proceeds in accordance with the formula for unimolecular reactions.

When germination does not take place at the temperature optimum, in consequence of which the process will be slower, again a period of induction is distinctly noticeable. At  $50^{\circ}$  there was not any decrease of the resistance, throughout the whole experiment.

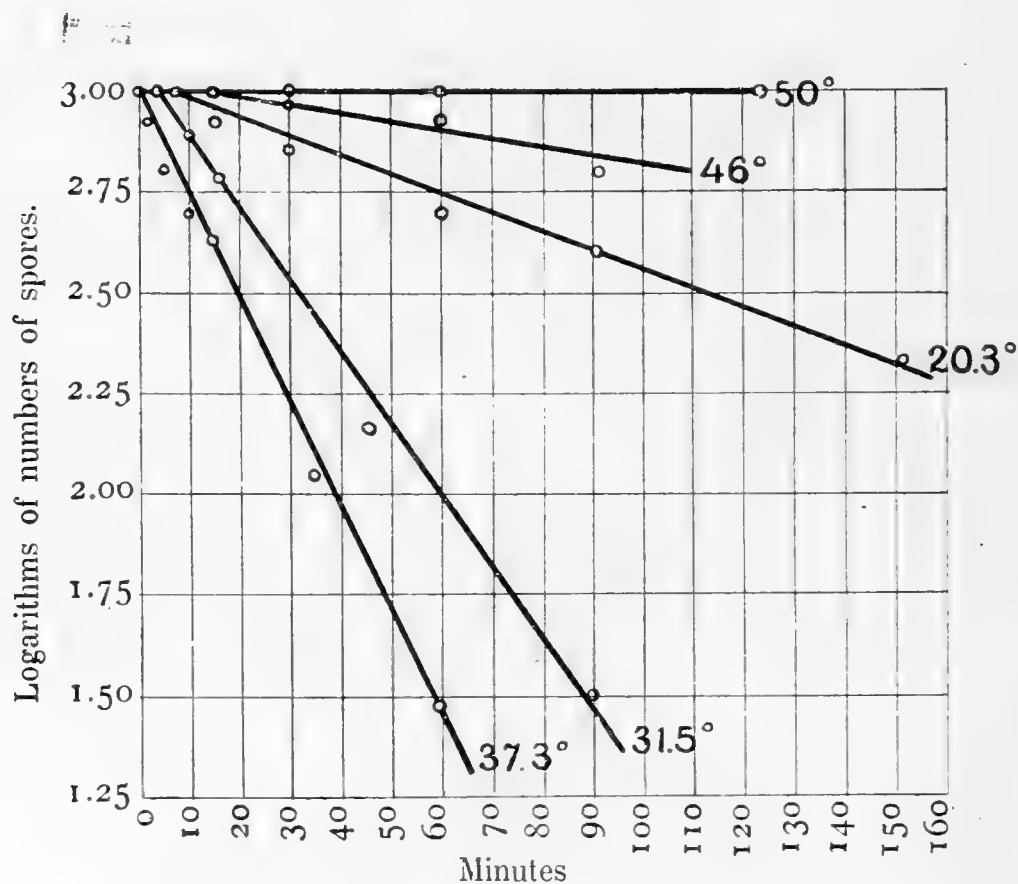


Fig. 9. Large spores in broth at  $20.3^{\circ}$ ,  $31.5^{\circ}$ ,  $37.3^{\circ}$ ,  $46^{\circ}$  and  $50^{\circ}$ .

The results of one experiment are tabulated in Table IV. Before plating the samples were heated for about five minutes up to  $78^{\circ}$ .

TABLE IV. Germination of large spores at 31.5°.

Time (min.)	Numbers on plates				Mean	Starting	
	1	2	3	4		number	$\log_{10}$ 1000
1	489	541	560	534	531	1000	3.000
5	476	583	492	541	523	985	2.993
15	313	340	347	319	330	621	2.793
45	76	90	77	74	79	149	2.173
90	18	16	14	19	17	32	1.505

The results obtained with small spores were entirely analogous with the above. In Fig. 10 the logarithms of the numbers are plotted against time.

On the other hand anthrax spores behave differently as shown in the curves of Fig. 11.

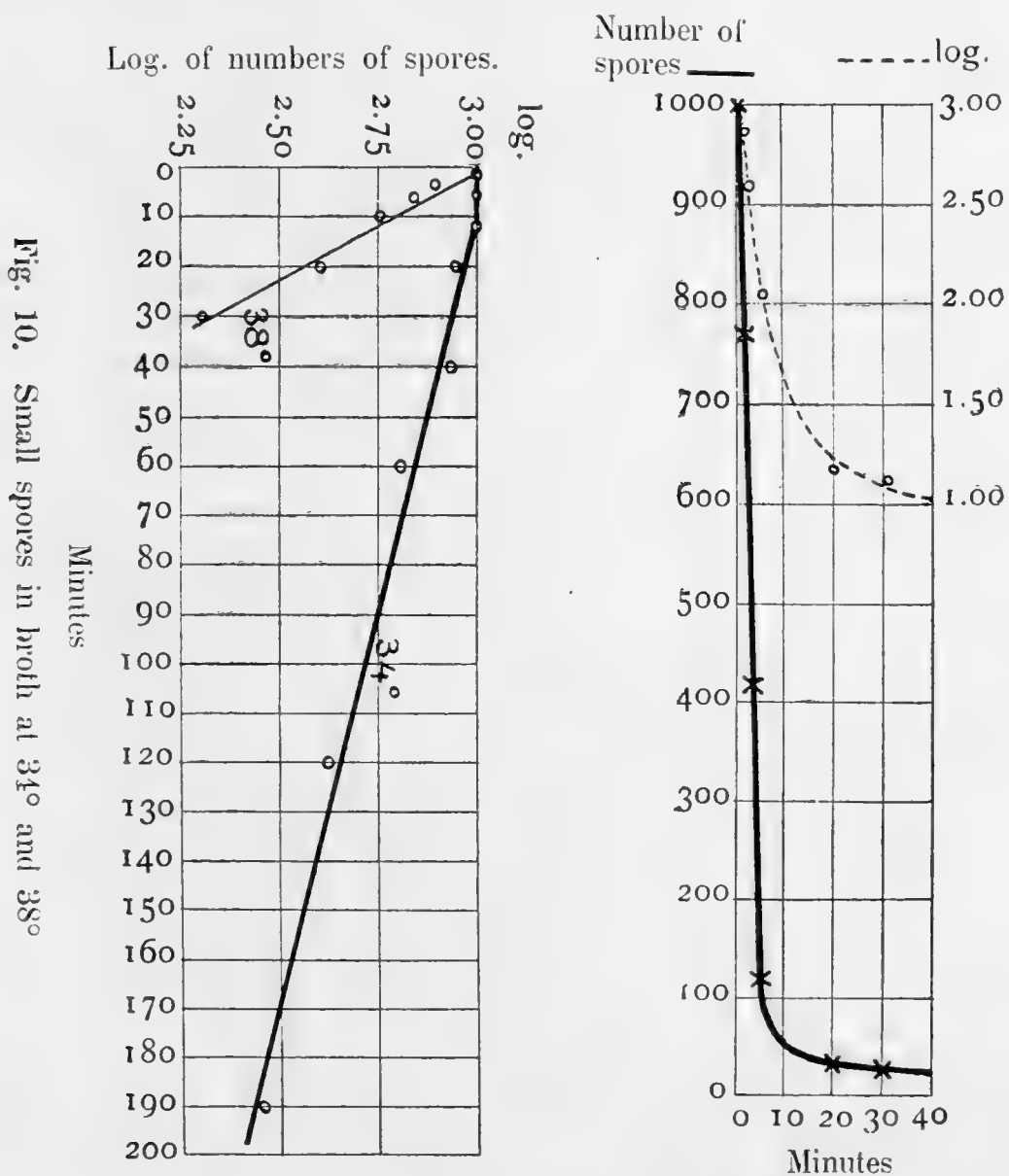


Fig. 11. Anthrax spores in broth at 34°.

The experiments taught that the value of  $k$  is not well nigh constant, but diminishes progressively, so that the logarithmic curve is convex on the side of the abscissae. (Fig. 11).

Since it was evident from Fig. 1 that anthrax spores were vulnerable at a temperature of  $80^\circ$ , the samples were heated up before plating to  $70^\circ$  only.

### III. *Conclusions.*

1. As regards disinfection of micro-organisms (vegetative forms as well as spores) some species are killed off in an orderly progress analogous to the process of a unimolecular reaction.

In the case of other species the velocity of disinfection is not constant, but either decreases or increases in the course of the process. However with them a certain regularity is also to be observed, viz. apart from the period of induction, the value of  $k$  alters in the same experiment continuously in the same sense.

Most often every species has a definite type expressing the orderly progress of its disinfection. Some there are however affording different types in different cultures of the same species; for this variability no satisfactory interpretation can be given.

It is still a matter of doubt, whether the progress of disinfection is chiefly a physico-chemic phenomenon, or whether differing individual resistance of micro-organisms of the same culture play a principal part in the process.

2. A striking analogy is to be observed in the orderly progress

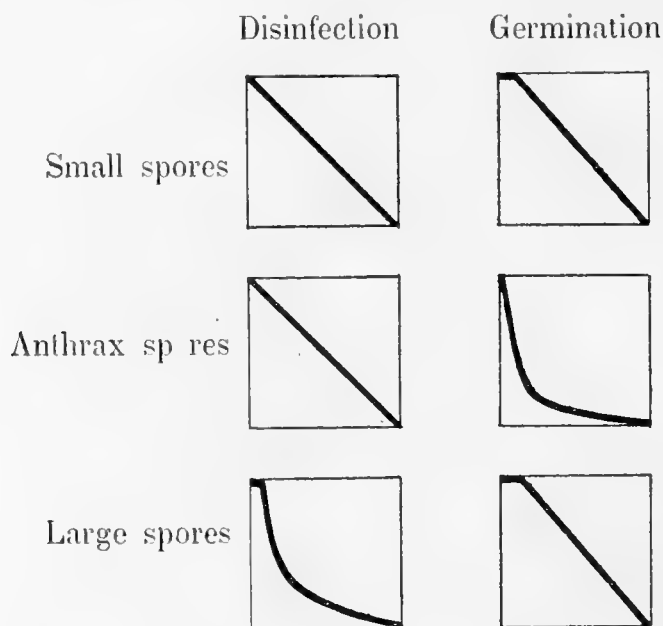


Fig. 12. Types of logarithmic curves.



of germination of spores to that of disinfection. Three species were examined. With two of them development took place in accordance with the formula of the unimolecular reactions.

The reaction-(germinating) velocity of the third species however was not constant, but decreased progressively.

For the same species the orderly progress of disinfection and germination do not always agree as to their types (fig. 12).

**Physics.** — “*On the second virial coefficient for monatomic gases, and for hydrogen below the BOYLE-point*”. By W. H. KEESOM. Supplement N<sup>o</sup>. 26 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

§ 1. *Introduction.* In Suppl. N<sup>o</sup>. 25 (Sept. '12) a comparison was made between the experimental data at present available concerning the second virial coefficient,  $B$ , for monatomic gases, and the relations for the variation of  $B$  with temperature deduced in Suppl. N<sup>o</sup>. 24 (June '12) from certain definite assumptions concerning the structure and the mode of action of the molecules. In continuation of that investigation the present paper supplies a similar comparison for the monatomic gases, and also, in view of the correspondence obtained in § 3*d* of Suppl. No. 25 between these gases and hydrogen below the BOYLE-point, for hydrogen, too, in that region of temperature. Until such time as the theories introduced by NERNST and EINSTEIN concerning the application of the quantum hypothesis to the rotations of the molecules have been further developed, only the suppositions made in Suppl. No. 24*b* § 5 are of any account as simplified assumptions if the specific heats of those gases are taken into account; according to those assumptions the molecules behave as if they were smooth rigid spheres of central structure, attracting one another with a force which is a function of the distance between their centres and is directed along the line joining their centres. As was done towards the end of § 5 of Suppl. No. 24*b*, this function is more closely specified by assuming that the attraction potential may be put equal to  $-r^{-q}$  where  $q$  is a constant <sup>1)</sup>. It

<sup>1)</sup> For the present comparison is postponed with the assumption made by TANNER, Diss. Basel 1912, in which, for simplicity, the action of the attractive force is supposed to be completely localised in a thin concentric spherical shell surrounding the molecule supposed spherical.

is true that without further evidence one is rather disinclined to regard such a distance law for the attraction potential as a fundamental property of the monatomic atom, and, should agreement with experiment be obtained with any definite value of  $q$ , one would like to obtain a deeper insight into the structure of the atom which would lead to the same law of distance for the resultant of the probable electric forces originating at various points of the atom; yet it is still clear that the results eventually obtained in the present paper for the index  $q$  can give important indications of the direction in which one must look for the development of the correct atomic model.

§ 2. A comparison was first made between the experimental data and the hypothesis of rigid spheres of central structure exerting central attractive forces upon one another proportional to  $r^{-(q+1)}$  where  $q$  is a constant (potential energy proportional to  $-r^{-q}$ ). This was done, following § 2 of Suppl. No. 25, by moving the  $\log B_N$ ,  $\log T$ -diagram for the experimental substance over the  $\mathcal{F}_3$ ,  $\log hv$ -diagram, where, following equation (42) of Suppl. No. 24b,

$$\mathcal{F}_3 = \log \left\{ 1 - \frac{3}{q-3} hv - \frac{1}{2!} \frac{3}{2q-3} (hv)^2 - \frac{1}{3!} \frac{3}{3q-3} (hv)^3 \dots \right\}. \quad (1)$$

For the meaning of  $h$  and  $v$  reference may be made to § 5 of Suppl. No. 24b. The scale was again 0.005 to the mm. and  $\log hv$  was again drawn increasing in the direction opposite to that in which  $\log T$  increases.

In this connection it is to be noted that when  $q$  is just slightly greater than 3, and then  $v$  must be taken small in comparison, the terms of equation (1) involving the square and higher powers of  $hv$  are small in comparison with the preceding term. The variation of  $B$  with temperature then becomes the same as in the case of the assumption of constant  $a_w$  and  $b_w$ . Hence comparison of experiment with the hypothesis of constant values of  $a_w$  and  $b_w$  can be made the same as comparison with the present assumption concerning the attraction potential with a value for  $q$  which is but slightly greater than 3.

### § 3. Argon, and hydrogen below the BOYLE-point.

a. In the case of argon <sup>1)</sup> the deviations of the experimental points

<sup>1)</sup> As in Suppl. No. 25 § 3d the individual virial coefficients of Comm. No. 118b have been used. In Comm. No. 128, June 1912, KAMERLINGH ONNES and CROMMELIN gave values of  $B_{A(71)}$  adjusted according to the temperature polynomial of the empirical equation of state; in these were included the lowest three temperatures, for which only a few points of the isotherms were observed and for which, individually, no sufficiently reliable values for the coefficients could be calculated; these, therefore, must be regarded as known with less certainty than

from the curves for  $q$  slightly greater than 3 ( $a_w$  and  $b_w$  const.), for  $q=4$ , and for  $q=5$  were all found to be relatively small. With the experimental material at present available for this gas it is difficult to settle the question as to which of these three values gives the best agreement (cf. Fig. 1). An extension of the temperature region for which  $B$  is known for argon, particularly towards the region of lower temperatures, as is already contemplated by KAMERLINGH ONNES and CROMMELIN, will be (cf. Fig. 1) of the greatest assistance in settling the point.

b. From Fig. 1<sup>1)</sup> it is evident that the best agreement is obtained for hydrogen below the BOYLE-point (see in particular the points representing the lowest three temperatures) on putting  $q=4$ . (Compare fig. 1 of Suppl. N<sup>o</sup>. 25, on which may be placed fig. 3 of the same

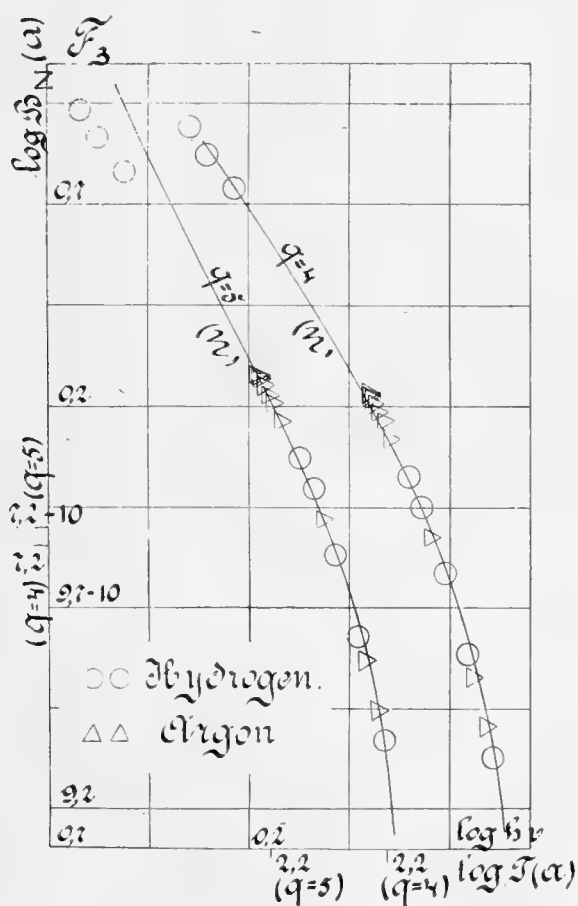


Fig. 1

paper for the argon points so as to exhibit the degree of agreement for  $q$  slightly greater than 3). Hence, as far as  $B$  is concerned, the behaviour of hydrogen below the BOYLE-point appears to be in pretty good agreement with the assumption of rigid spheres of central structure with an attraction potential<sup>2)</sup> proportional to  $-r^{-4}$ .

If we assume that, as far as  $B$  is concerned, hydrogen behaves in a manner similar to the monatomic argon not only (as in Suppl. N<sup>o</sup>. 25 § 3d) within that region of temperature corresponding to the respective observational region for argon, but also towards lower temperatures, so that the series of argon points may be supplemented by means of

the others. As the calculations of the present paper may be regarded as another method of adjusting the virial coefficients, it seemed more reasonable to effect a direct comparison of the equation with the individual values. Comparison of the deviations occurring in this method which are independent of the adjustment to the empirical temperature polynomial, with those obtained by the latter method can then afford a basis of judging whether the deviations are greater or less than the degree of accuracy of the observations (cf. p. 646 note 1).

1) In this the point  $\log T = 2,0$ ,  $\log B_N = 6,5 - 10$  for  $H_2$  coincides with the point  $\log h\nu = 9,551 - 10$ ,  $\mathcal{F}_3 = 9,488 - 10$  when  $q = 4$ , and with the point  $\log h\nu = 9,815 - 10$ ,  $\mathcal{F}_3 = 9,495 - 10$  when  $q = 5$ .

2) BRAAK, Diss. Leiden 1908, p. 85, finds for  $H_2$  at these low temperatures a

hydrogen below the BOYLE-point, then it follows from fig. 1<sup>1)</sup> that the attraction potential for argon is also proportional to  $-r^{-4}$ ; but this conclusion must always be subject to reserve concerning the validity of the assumption just made down to the lowest temperatures, which has not yet been submitted to the test of experiment in the present case.

c. Following § 6 of Suppl. N<sup>o</sup>. 25, the accompanying table gives the temperature variation of  $\eta T^{-1/2}$  ( $\eta$  is the coefficient of viscosity) as given by the measurements of KOPSCH<sup>2)</sup> compared with values of  $b_W^{-1}$  from

$$b_W = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \cdot e^{h\nu} \dots \dots \dots (2)$$

The latter relation appears on the separation of the attraction virial from the collision virial, as is indicated in equation (41) of Suppl. N<sup>o</sup>. 24b. For  $v$  the value  $1.46 \cdot 10^{-14}$  is taken from the data given on p. 645 note 1 for the superposition of the diagram for H<sub>2</sub>, A upon that for the attraction potential  $-r^{-q}$  with  $q = 4$  (for the relative positions of the H<sub>2</sub> and the A diagrams see p. 425 note 3 of Suppl. N<sup>o</sup>. 25).

$t$	$\frac{\eta}{\eta_{00C}} \sqrt{\frac{T_{00C}}{T}}$ argon	$\frac{b_{W00C}}{b_W}$ attraction potential $-r^{-q}$ $v = 1.46 \cdot 10^{-14}$
0	1.000	1.000
— 40.17	0.949	0.927
— 78.82	0.883	0.836
— 132.30	0.729	0.660
— 183.17	0.606	0.406

corresponding value for the index of  $r$  in the law of distance governing the force. From the ratio of the potential (heat of expansion) to the virial, REINGANUM, Ann. d. Phys. (4) 6 (1901), p. 546, deduces that the force is proportional to from  $r^{-4}$  to  $r^{-5}$ .

1) The deviations of the individual values of  $B_N$  from  $q = 4$  are of the same order of magnitude and are throughout in the same sense as their deviation from the values adjusted according to the empirical temperature polynomial.

2) W. KOPSCH. Diss. Halle 1909.

Comparison of the second and third columns would lead one to desire a smaller value for  $\nu$ , and this in turn would lead one to fix<sup>1)</sup> the index  $q$  more closely as lying between 3 and 4, but nearer 4 than 3<sup>2)</sup>. (Reference should be made, however, to the reserve of § 6 of Suppl. N<sup>o</sup>. 25 qualifying the validity of these conclusions drawn from the influence of molecular attraction upon viscosity).

*d.* The  $\log B$ ,  $\log T$ -diagram for argon could not be made to coincide with the curve for constant doublets (Suppl. No. 25 § 3 *c*); this is in agreement with § 3 *d* and *e* of Suppl. No. 25 (and in particular with Figs. 2 and 3 of that paper) and also with the known caloric behaviour of this substance.

§ 4. *Helium*<sup>3)</sup>. Helium shows, at the higher temperatures, a deviation from all the hypotheses introduced in Suppl. No. 24 and tested in Suppl. No. 25 and in the present paper, for the maximum exhibited by  $B$  at these temperatures (cf. Figs. 15 and 16 of Suppl. No. 23, Math. Enc. V 10) is not given by any of these assumptions. It can well be that the peculiarity ascribed by KAMERLINGH ONNES to the helium atom at low temperatures is also present at these higher temperatures, so that one would have to assume the helium atom to be compressible, or to assume a relatively large increase in the attraction (cf. also note 4 on this page).

Moreover, the points for the lowest three temperatures cannot be regarded as known with the same degree of certainty as the others.

From both these circumstances it follows that the moving of the helium diagram over that for rigid spheres with an attraction potential  $\frac{1}{r^q}$  ( $q = \text{const.}$ ) can be made to take place in a manner to a very large extent quite arbitrary. Fig. 2 shows a superposition for the case  $q = 4$ . In this the point  $\log T = 1,3$ ,  $\log B_N = 6,5 - 10$  coincides with the point  $\log hv = 9,478 - 10$ ,  $\mathcal{F}_3 = 9,688 - 10$ .

With the exception of the highest temperatures<sup>4)</sup> the coincidence is

1) The data given in note 1 p. 645 for the superposition in Fig. 1 would yield  $\nu = 2,68 \cdot 10^{-14}$  for  $q = 5$ .

2) Cf. also C. BRAAK, loc. cit. p. 645 note 2.

3) The individual virial coefficients for He are taken from Table II of Comm. No. 102*a* by KAMERLINGH ONNES; these are supplemented by the virial coefficients for  $-252,072$  and  $-258,082$  C., which have not yet been published but have kindly been placed at my disposal by Prof. KAMERLINGH ONNES (they have already been used for the construction of Figs. 15 and 16 of Suppl. No. 23) and also by the value for  $4,029$  K. taken from Comm. No. 119 §-5*b*.

4) At these temperatures Prof. KAMERLINGH ONNES tells me there is some uncertainty; improved values are being obtained.

not to be regarded as wholly bad, so that at the lower temperatures (below  $-100^{\circ}$  C.) the experimental results at present available for

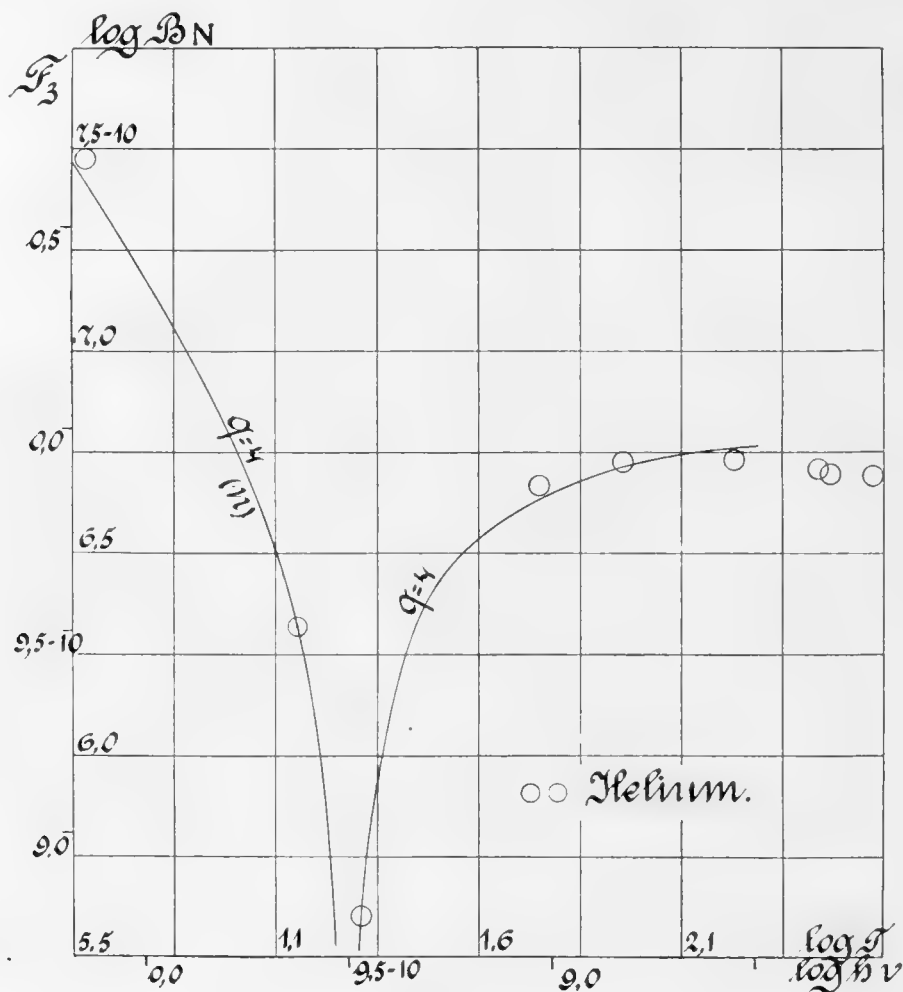


Fig. 2.

helium are, as far as  $B$  is concerned, compatible with the assumption of rigid spheres of central structure with an attraction potential proportional to  $-r^{-4}$ .

Having now reached the end of the considerations advanced in Suppl. N<sup>o</sup>. 24, 25, and 26 it is my pleasant duty to thank Prof. KAMERLINGH ONNES for having invited me to participate in the investigation of the second virial coefficient for gases of low critical temperature, which he had undertaken with the object of reaching some conclusion regarding the structure and mode of action of the molecule, in particular with the help afforded by the application of BOLTZMANN'S principles, and also for his kindness in leaving to me the continuation of the investigation within the particular region which I have treated in this series of papers.

**Physics.** — “*On the HALL effect, and the change in resistance in a magnetic field at low temperatures. III. Measurements at temperatures between  $+17^{\circ}$  C. and  $-200^{\circ}$  C. of the HALL effect, and of the change in the resistance of metals and alloys in a magnetic field*”. By BENGT BECKMAN. (Communicated by Prof. H. KAMERLINGH ONNES). Communication No. 130*a* from the Physical Laboratory of Leiden.

(Communicated in the meeting of September 28, 1912).

§ 1. *Introduction.* A communication was made by KAMERLINGH ONNES and the present writer to the meeting of June 29th 1912, of the results of measurements of the HALL-effect and of the increase of resistance in a magnetic field made by us at liquid hydrogen temperatures. In the present paper those results are extended to the temperatures which are obtainable with liquid ethylene and liquid oxygen, with the same experimental material and following the same experimental methods. It is of great importance that observations made with any particular substance should be distributed as uniformly as possible over the region of temperature under investigation. The measurements now completed make it possible for the results obtained at liquid hydrogen temperatures to be compared with those of former experimenters, who, without exception, proceed only to liquid air temperatures.

For a description of methods and material we may refer to the above Communication N<sup>o</sup>. 129*a*. In order to complete the diagrams of the present paper the results for liquid hydrogen temperatures in the paper quoted are also indicated without making specific mention of the fact on each occasion. The present paper is confined to a discussion of the results obtained with bismuth.

### *I. Bismuth.*

§ 2. *Change in the resistance of a wire of electrolytic bismuth.* The resistance of the bismuth wire  $B_{iH}$  was measured in eight different fields at five different temperatures:  $T = 290^{\circ}$  K,  $170^{\circ}$  K,  $139^{\circ}.5$  K,  $90^{\circ}$  K,  $72^{\circ}$  K. These results are given in Table I.  $H$  is the field strength in gauss,  $w'_T$  the resistance in ohms in the magnetic field at the absolute temperature  $T$ ,  $w_T$  the resistance without field at that temperature, and  $w_0$  the resistance without field at  $0^{\circ}$  C.

Fig. 1 shows the increase of resistance as a function of the field at constant temperature (Isotherms), and fig. 2 the increase of resistance as a function of the temperature under constant field (Isopedals).

TABLE I.

Resistance of  $Bi_{dI}$  as a function of the temperature and of the field.

$H$ in Gauss	$T = 290^\circ$		$T = 170^\circ$		$T = 139^\circ.5$		$T = 90^\circ$		$T = 72^\circ$	
	$w'$	$\frac{w'}{w_0}$	$w'$	$\frac{w'}{w_0}$	$w'$	$\frac{w'}{w_0}$	$w'$	$\frac{w'}{w_0}$	$w$	$\frac{w'}{w_0}$
0	2.570	1.057	1.570	0.646	1.365	0.562	1.075	0.442	0.989	0.407
2760	2.770	1.140	2.366	0.973	2.571	1.058	3.92	1.613	4.68	1.926
5540	3.110	1.280	3.657	1.504	4.414	1.816	9.24	3.80	12.28	5.052
7370	3.473	1.388	4.612	1.897	5.894	2.425	14.20	5.84	19.10	7.86
9200	3.635	1.495	5.613	2.310	7.605	3.128	19.74	8.12	26.6	10.94
11850	4.002	1.646	7.299	3.003	10.56	4.346	29.82	12.27	41.2	16.95
13600	4.248	1.746	8.506	3.500	12.596	5.180	38.60	15.88	52.4	21.6
15670	4.540	1.868	10.204	4.199	15.51	6.380	48.05	19.77	67.2	27.65
17080	—	—	11.412	4.695	17.78	7.316	55.80	22.96	77.8	32.0

In Table II are collected some results obtained by different experimenters for the increase of resistance in a magnetic field. It contains values of  $\frac{w_{83^\circ \text{ K}}}{w_{273^\circ \text{ K}}}$  and  $\frac{w'_T}{w_0}$  in a field of 16 kilogauss at the temperature of liquid air.

TABLE II.

Increase of resistance in a field of 16 kilogauss.

$\frac{w_{83^\circ}}{w_{273^\circ}}$	$T$	$\frac{w'}{w_0}$	Observer
0.42—0.44	81°K.	13.3	BLAKE <sup>1)</sup>
—	81°	18.3	BLAKE: 5b
—	83°	23.8	DU BOIS and WILLS <sup>2)</sup>
0.43	90°	20.9	BECKMAN
	72°	28.7	
0.36	88°	32	DEWAR and FLEMING <sup>3)</sup>

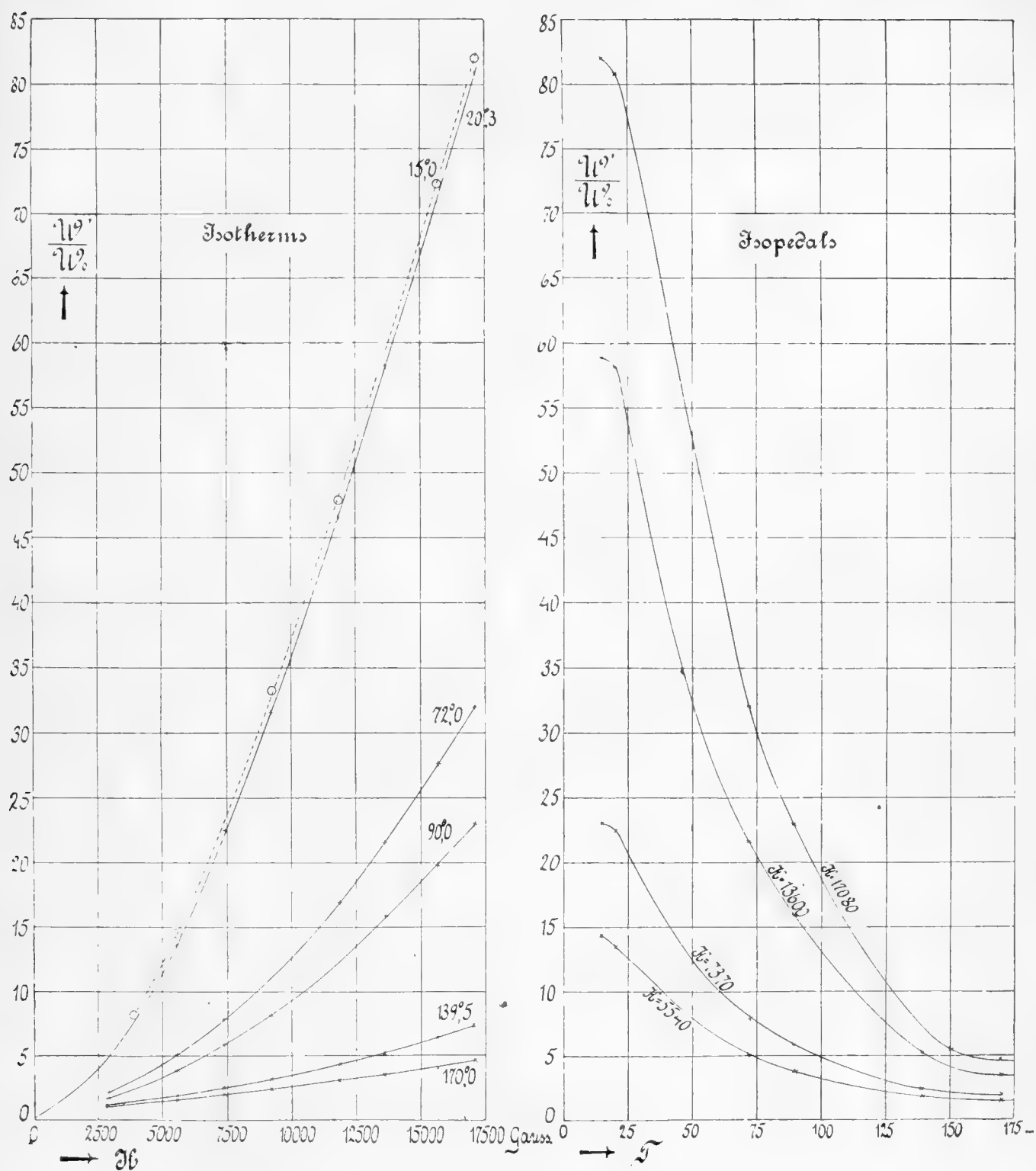
<sup>1)</sup> P. C. BLAKE: Ann. d. Physik. 28, 449, 1909.

<sup>2)</sup> H. DU BOIS and A. P. WILLS: Verh. d. Deutsch. Phys. Ges. I, 169, 1899.

<sup>3)</sup> J. DEWAR and J. A. FLEMING: Proc. Roy. Soc. 60, 72, 1896 and 425, 1897.



Fig. 1 and 2.



The measurements by DEWAR and FLEMING give the largest results for  $\frac{w'}{w_0}$  and at the same time the smallest results for  $\frac{w_{33^\circ \text{K}}}{w_{273^\circ \text{K}}}$ . They were probably obtained with extremely pure material. BLAKE worked with a large number of different bismuth wires. One of these, labelled 5b, gave a larger value for  $\frac{w'}{w_0}$  than the others for which he gives a mean value. The wire with which I worked gives exactly this

mean value for  $\frac{w_{83^\circ \text{K}}}{w_{273^\circ \text{K}}}$ , but a greater value for  $\frac{w'}{w_0}$  at the temperature of liquid air. At higher temperatures there is also agreement between BLAKE'S values for the latter ratio and mine.

The maximum in the isopedals found by BLAKE to lie at 36600 gauss at the temperature  $T = 99^\circ \text{K}$ . and which, for lower temperatures, ought to be found at lower fields, was not observed in the present experiments.

In the weaker fields the isotherms are convex towards the axis of abscissae; from 12 Kilogauss upwards they become straight. For  $H > 12000$  the relationship

$$\frac{w'}{w} = aH + b \quad . . . . . (1)$$

holds, where  $a$  and  $b$  are constants, while, at lower temperatures

$$a = a_0 e^{-\beta T} \quad . . . . . (2)$$

to a first approximation. The following Table shows to what degree of approximation this relationship holds.

TABLE III.

 $a$  for  $Bi_{dF}$ 

$T$	$a_{obs.}$	$a_{calc.}$
170	1.94	1.95
139.5	4.2	4.5
90	18.3	17.1
72	29.7	27.9
20	117.5	114
15	121	131

Even at the boiling point of oxygen  $b$  is already clearly negative — 26.5). As the temperature falls the absolute value of  $|b|$  increases rapidly, and at hydrogen temperatures it reaches the value — 110.

§ 3. *The HALL effect and the increase of resistance of plates of compressed electrolytic bismuth.* Tables IV and V contain the results of measurements made at ordinary temperature and at two liquid oxygen temperatures with the plates  $Bi_{pI}$  and  $Bi_{pII}$ .  $R$  is the HALL-

TABLE IV.

HALL effect, asymmetry and resistance change for  $Bi_{pI}$ .

$H$	$T = 289^\circ$						$T = 90^\circ$						$T = 74.5^\circ$						
	$RH$	$D$	$-R$	$\left[\frac{w}{w}\right]_T$	$RH$	$D$	$R$	$Q$	$\left[\frac{w}{w}\right]_T$	$RH$	$D$	$-R$	$Q$	$\left[\frac{w}{w}\right]_T$	$RH$	$D$	$-R$	$Q$	$\left[\frac{w}{w}\right]_T$
	2060	$13.9 \times 10^3$	$0.2 \times 10^3$	6.75	1.06	$43.8 \times 10^3$	$3.0 \times 10^3$	21.25	—	2.48	$54.3 \times 10^3$	$0.8 \times 10^3$	26.35	—	3.08	$54.3 \times 10^3$	$0.8 \times 10^3$	26.35	—
3450	20.9	0.1	6.06	1.12	63.5	5.7	18.4	—	3.84	72.7	8.9	21.05	—	5.17	72.7	8.9	21.05	—	5.17
5660	29.1	1.1	5.14	1.21	88.8	12.6	15.7	—	6.45	109.6	12.9	19.35	—	9.16	109.6	12.9	19.35	—	9.16
7160	33.2	0	4.64	1.29	105.7	17.2	14.75	2.3	8.50	136	25.7	19.0	2.3	12.3	136	25.7	19.0	2.3	12.3
9880	40.3	0.9	4.08	1.45	142.6	33	14.45	2.7	13.10	190.2	42.7	19.25	2.3	19.45	190.2	42.7	19.25	2.3	19.45
11090	42.6	1.1	3.84	1.50	—	—	—	—	—	215	52	19.4	2.4	23.0	215	52	19.4	2.4	23.0
0	$w_{289^\circ} = 0.00209 \Omega$						$w_{90^\circ} = 0.00097 \Omega$						$w_{74.5^\circ} = 0.00088 \Omega$						

TABLE V.  
Hall effect, asymmetry and resistance change for  $B_{\perp} p_{II}$

$H$	$T = 289^{\circ}$					$T = 93^{\circ}$					$T = 73^{\circ}$				
	$RH$	$D$	$-R$	$\left[\frac{w'}{w}\right]_T$	$\left[\frac{w'}{w}\right]_T$	$RH$	$D$	$-R$	$Q$	$\left[\frac{w'}{w}\right]_T$	$\left[\frac{w'}{w}\right]_T$	$RH$	$D$	$-R$	$Q$
2060	$18.7 \times 10^3$	$0.1 \times 10^3$	9.08	1.023	74.3	$0.9 \times 10^3$	36.1	—	1.295	94.4	$1.3 \times 10^3$	45.8	—	1.386	
3450	28.2	0.1	8.17	1.057	110.7	1.5	32.1	—	1.59	139.5	3.5	40.4	—	1.727	
5660	39.8	0.2	7.05	1.108	155.2	6.2	27.4	—	—	205	8.5	36.2	—	2.355	
7160	46.1	0.2	6.44	1.148	185.8	10	25.95	0.68	2.47	248	13.7	34.6	0.76	2.787	
8520	52.1	0.4	6.12	1.186	214.2	14	25.15	0.74	2.89	289	16.5	33.9	0.73	3.255	
9880	55.9	0.1	5.66	1.222	243.0	18	24.6	0.79	3.28	330.5	20.5	33.5	0.75	3.718	
11090	59.9	0.4	5.41	1.260	267.3	22	24.1	0.82	3.67	367	24.2	33.1	0.78	4.12	
12090	62.8	0.7	5.19	1.287	288.0	24	23.8	0.82	3.94	398	28.5	32.9	0.82	4.483	
0	$w_{289^{\circ}} = 0.00389 \Omega$					$w_{93^{\circ}} = 0.00444 \Omega$					$w_{73^{\circ}} = 0.00455 \Omega$				

coefficient in *C. G. S.* units, *D* is the asymmetry and *Q* is the quantity

$$\frac{D}{\frac{w'}{w} - 1}$$

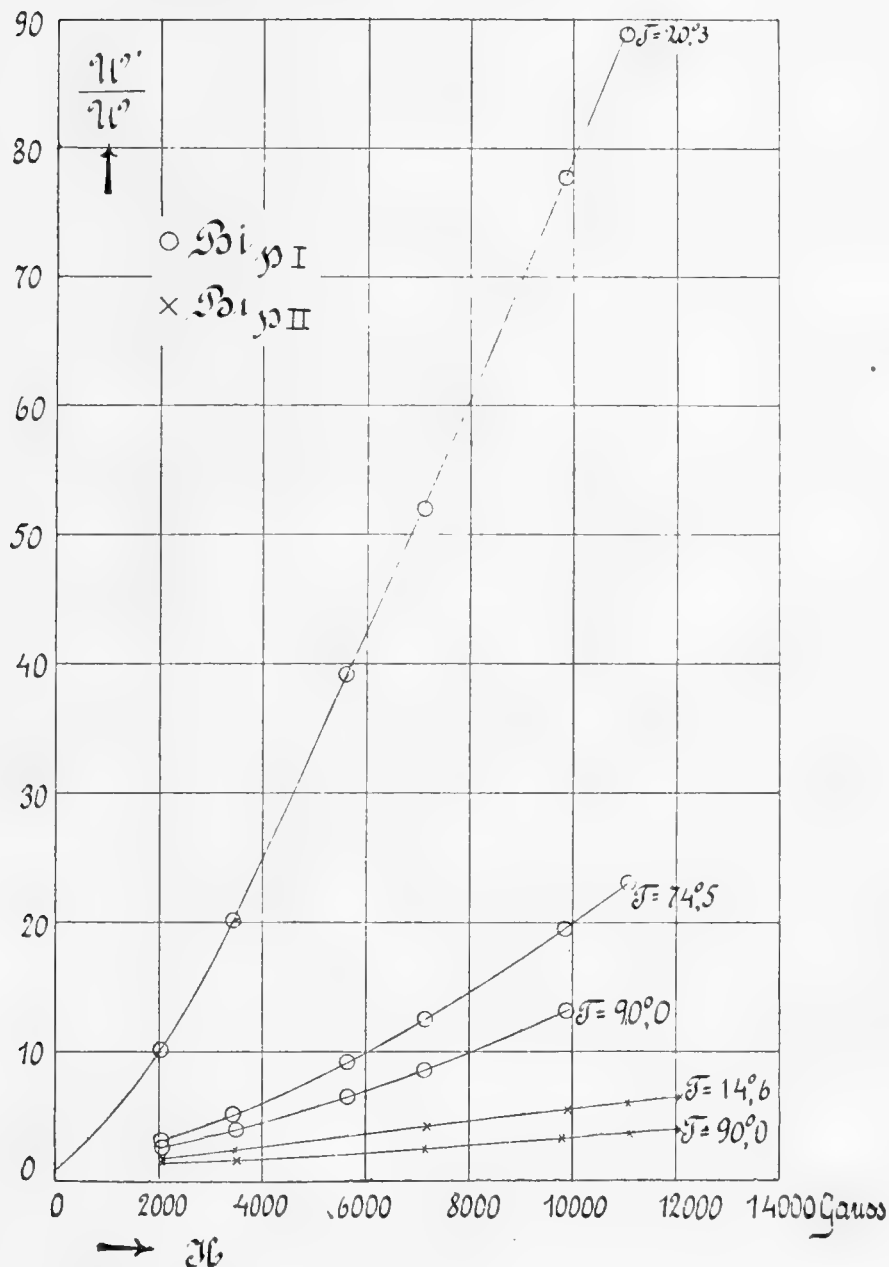


Fig. 3.

Figs. 3 and 4 show the resistance increase, and fig. 5 the HALL effect as functions of the field for various temperatures<sup>1)</sup>.

The isotherms of the magnetic increase of resistance are of the same nature as those for  $Bi_{3pI}$ , but the rectilinear portion of the curve now begins at 7 kilogauss. Equation (2) also holds in this case

<sup>1)</sup> Remembering that  $RH = \frac{Ed}{I}$  where  $E$  is the HALL potential difference,  $d$  the thickness of the plate, and  $I$  the main current, we see that  $RH$  is the HALL potential difference for  $d = 1$  and  $I = 1$ .

for the region  $90^\circ K \leq T < 15^\circ K$ . This is evident from Table VI.

The diminution of the resistance at low temperatures without a magnetic field is practically the same for both  $Bi_{pI}$  and  $Bi_{dI}$ .

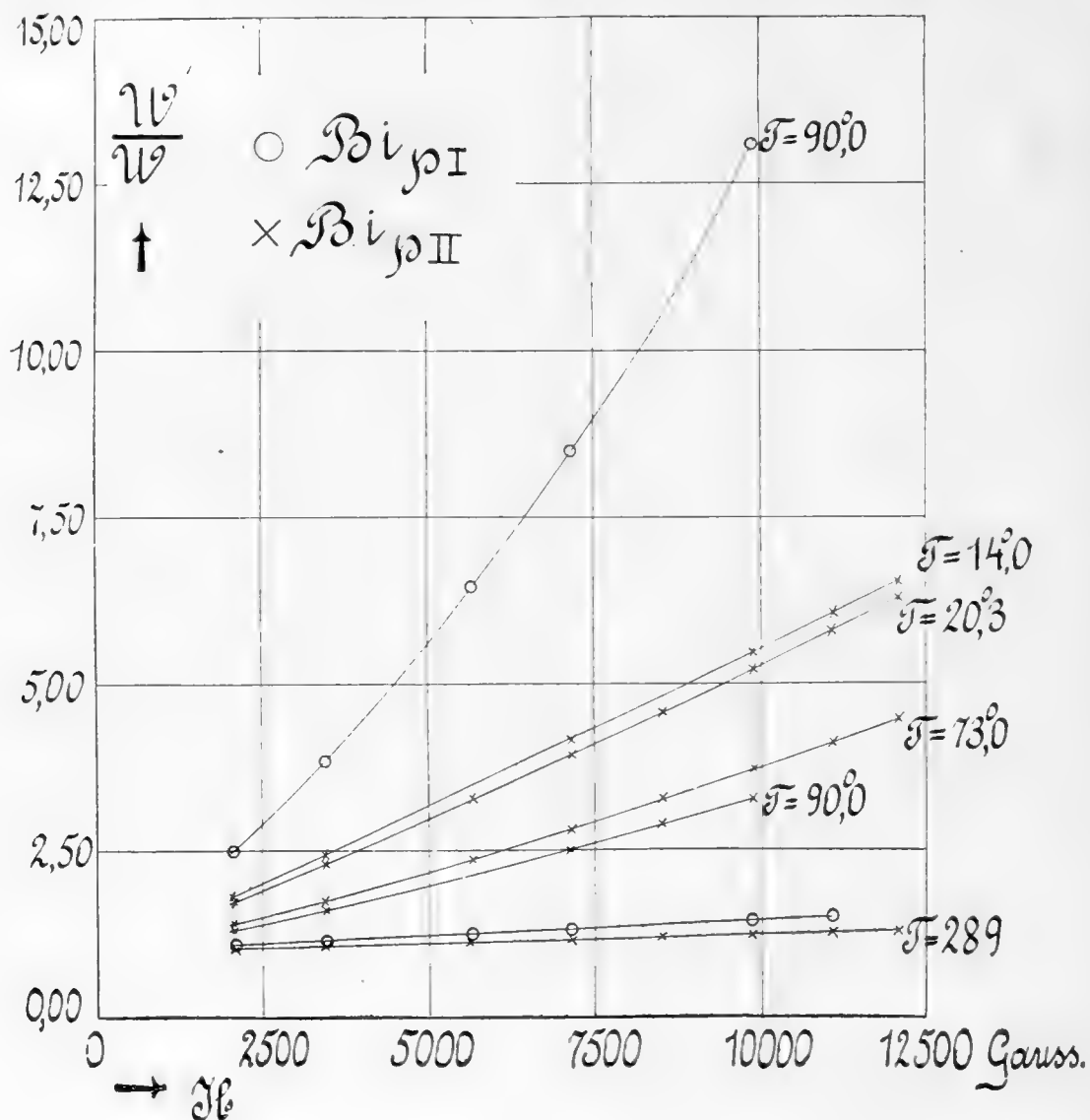


Fig. 4.

TABLE VI.

$a$  for  $Bi$ .

$T$	$Bi_{pI}$		$Bi_{pII}$	
	$a_{obs}$	$a_{calc.}$	$T$	$a_{obs.}   a_{calc.}$
90	1.69	1.77	$90^\circ$	29.3   31
74.5	2.7	2.55	$73^\circ$	35.8   34.4
20.3	9.2	9.1	$20^\circ.3$	47.3   47.3
			14.6	48.3   49

In liquid air the magnetic increase of resistance, however, appears to be much greater for  $Bi_{dI}$ , just as was found to be the case in liquid hydrogen<sup>1)</sup>.

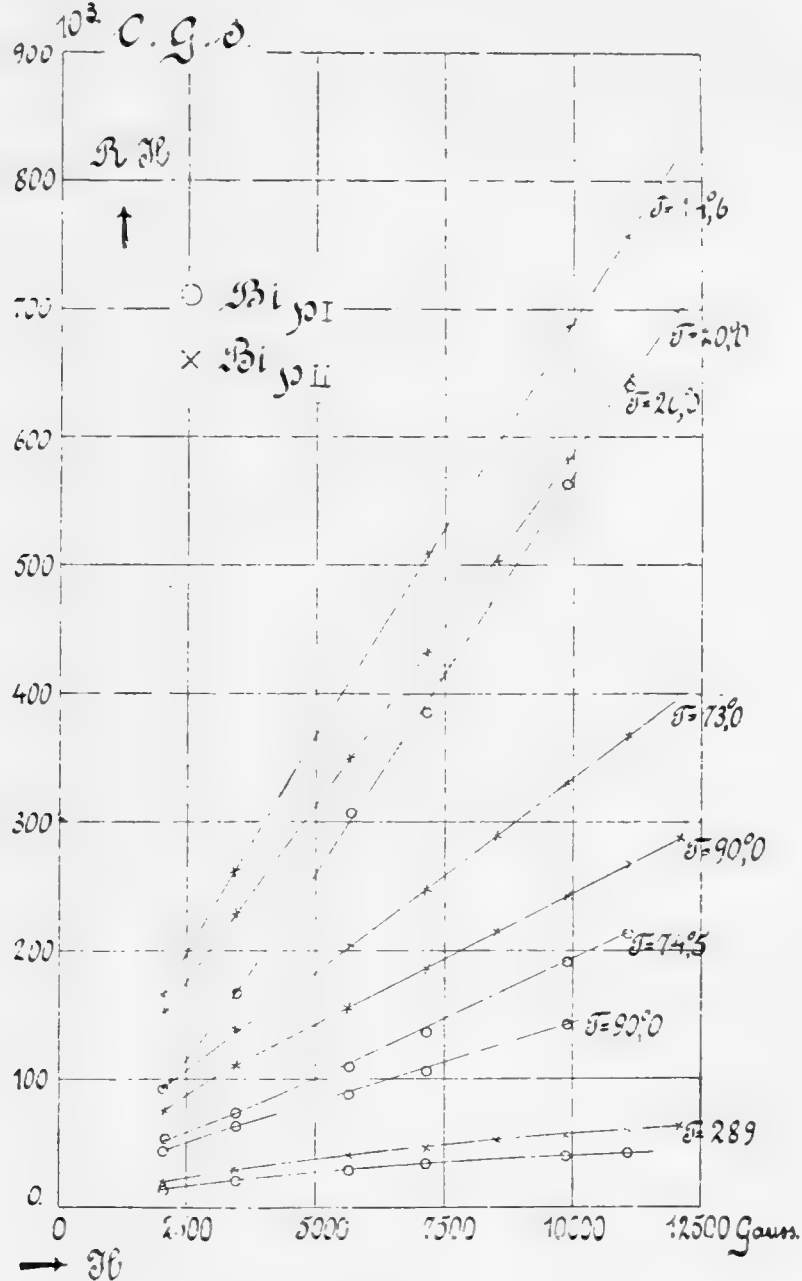


Fig. 5.

For  $H = 11090$  we find at

	$Bi_{dI}$	$Bi_{pI}$	$Bi_{pII}$
$T = 90^\circ K$	$\frac{w'}{w_0} = 11,6$	7,5	3,25
$T = 20,3^\circ K$	$\frac{w'}{w_0} = 42$	19,7	4,7

For  $Bi_{pII}$  the resistance temperature coefficient with no magnetic field is negative, which undoubtedly points to the presence of impurity.

At  $T = 289^\circ K$  the specific resistance of  $Bi_{pI}$  is about  $1,5 \times 10^5$ , and for  $Bi_{pII}$   $2,3 \times 10^5$  C.G.S.

<sup>1)</sup> H. KAMERLINGH ONNES and BENGT BECKMAN, Comm. N<sup>o</sup>. 129a

The magnetic change of resistance is much smaller for  $Bi_{\rho II}$  particularly so at low temperatures.

Just as in the experiments in liquid hydrogen, for  $H > 3000$ ,  $RH$  becomes a linear function of the field

$$RH = a' H + b' \dots \dots \dots (3)$$

Following J. BECQUEREL<sup>1)</sup> we may regard the HALL-effect for bismuth as resulting from two components. One of these is proportional to the field, and was always negative for the plates ( $Bi_{\rho I}$ ,  $Bi_{\rho II}$ ) I used. The other is constant or, as one may say, saturated, for these plates from  $H = 3000$  upwards.

Within the temperature region

$$90^\circ K \geq T > 15^\circ K$$

$a'$  can, to a first approximation, be satisfactorily represented by

$$a' = a_0' e^{-\beta T} \dots \dots \dots (4)$$

The agreement for  $T = 90^\circ K$  between observation and calculation from (3) with  $a' = 20.6$  and  $b' = 39,3 \times 10^3$  for the plate  $Bi_{\rho II}$  is exhibited in Table VII, while Table VIII shows how far the relationship (4) holds.

T A B L E VII.		
Linear variation of the HALL effect in strong fields for $Bi_{\rho II}$ at $T = 90^\circ K$ .		
$H$	$RH_{obs.}$	$RH_{calc.}$
3450	$110.7 \times 10^3$	$110.4 \times 10^3$
5660	155.2	155.8
7160	185.8	186.8
8520	214.2	214.8
9880	243.0	242.8
11090	267.3	267.8
12090	288.0	288.3

The constant  $b'$  which gives the value of the second component of the effect in the state of saturation is commonly negative. Only for  $Bi_{\rho I}$  at hydrogen temperatures does it become positive. With

<sup>1)</sup> J. BECQUEREL: C. R. 154, 1795, 1912.



$Bi_{pII}$   $b'$  is almost constant for  $T \leq 90^\circ$ ; with  $Bi_{pI}$   $b'$  is very small and for  $T \geq 72^\circ$   $K$  is practically constant.

In strong fields the constant  $R$  approaches a limiting value in

T A B L E VIII.					
$a'$ for $Bi_{pI}$			$a'$ for $Bi_{pII}$		
$T$	$a'_{obs.}$	$a'_{calc.}$	$T$	$a'_{obs.}$	$a'_{calc.}$
90°	12.4	12.1	90°	20.6	22.0
74.5	17.7	17.4	73°	29.8	27.6
20.3	62.1	62.6	20.3	54.3	57.3
			14.6	64.5	62.4

accordance with equation (3). In weak fields  $RH$  for  $Bi_{pI}$ , is inversely proportional to the temperature at  $T = 289^\circ K$ ,  $90^\circ K$ ,  $74.5^\circ K$ .

Tables IV and V also contain the quantity  $Q = \frac{D}{\frac{w'}{w} - 1}$ . For  $H > 7000$ ,  $Q$  is either a linear function of the field, or a constant<sup>1)</sup>.

**Physics.** — “On the HALL effect and the change in resistance in a magnetic field at low temperatures. IV. Measurements at temperatures between  $+17^\circ$  C. and  $-200^\circ$  C. of the HALL effect, and of the change in the resistance of metals and alloys in a magnetic field.” By BENGT BECKMAN. Communication N<sup>o</sup>. 130b from the Physical Laboratory at Leiden. (Communicated by Prof. KAMERLINGH ONNES).

(This Communication is a continuation of Comm. N<sup>o</sup> 130a in which the behaviour of bismuth was discussed.)

## II. Gold, Silver, Copper, Palladium.

§ 4. HALL effect for Gold. From the temperature decrease of the resistance without magnetic field<sup>2)</sup>,  $\frac{w_{T=20}}{w_{T=290}} = 0,035$ , it is to be supposed that this plate is composed of purer gold than that of the wire

<sup>1)</sup> Cf. E. v. EVERDINGEN, Leiden Communications Suppl. no. 2. p. 57.

<sup>2)</sup> H. KAMERLINGH ONNES and BENGT BECKMAN.; Comm. N<sup>o</sup>. 129a.

$Au_0$  of Comm. N°. 99, which was known to contain 0,03 % impurity. The thickness of the plate was 0,101 mm.

TABLE IX.								
HALL effect for Gold $Au_{pI}$ .								
$T = 290^\circ \text{K.}$			$T = 90^\circ \text{K.}$			$T = 77^\circ \text{K.}$		
$H$	$RH$	$-R \times 10^4$	$H$	$RH$	$-R \times 10^4$	$H$	$RH$	$-R \times 10^4$
7730	5.62	7.27	7730	5.82	7.53	4940	3.75	7.59
9500	6.75	7.11	9500	7.24	7.62	9065	6.95	7.67
11080	8.11	7.32	11080	8.53	7.70	10270	7.72	7.59
12200	8.85	7.25	12200	9.24	7.58			
$w_{290^\circ} = 2.2 \times 10^{-6} \Omega$			$w_{90^\circ} = 54,6 \times 10^{-6} \Omega$					

§ 5. HALL effect for Silver. The plate  $Ag_{pI}$  was found to be of practically the same purity as that of the wire  $Ag_I$  of Comm. N°. 92 which contained 0,18 % impurity. The thickness of the plate was 0,096 mm.

TABLE X.				
HALL effect for Silver $Ag_{pI}$ .				
$T = 290^\circ \text{K.}$			$T = 90^\circ \text{K.}$	
$H$	$RH$	$-R \times 10^4$	$RH$	$-R \times 10^4$
4940	3.97	8.04	4.10	8.30
7260	5.81	8.01	5.92	8.15
9065	7.23	7.98	7.45	8.22
10270	8.16	7.95	8.38	8.16
$w_{290^\circ} = 173 \times 10^{-6} \Omega$			$w_{90^\circ} = 37 \times 10^{-6} \Omega$	

§ 6. HALL effect for electrolytic Copper. The thickness of the plate  $Cu_{pI}$  was 0.057 mm.

TABLE XI. HALL effect for Copper $Cu_{pl}$ .				
$H$	$T = 290^\circ \text{K.}$		$T = 90^\circ \text{K.}$	
	$RH$	$-R \times 10^4$	$RH$	$-R \times 10^4$
7260	3.59	4.95	4.05	5.58
9065	4.42	4.87	5.04	5.56
10270	5.08	4.95	5.66	5.51
		$w_{290^\circ} = 312 \times 10^{-6} \Omega$	$w_{90^\circ} = 54 \times 10^{-6} \Omega$	

§ 7. HALL effect for Palladium. The thickness of the plate was 0,100 mm.

TABLE XII. HALL effect for palladium $Pd_{pl}$ .					
$T = 290^\circ \text{K.}$			$T = 90^\circ \text{K.}$		
$H$	$RH$	$-R \times 10^4$	$H$	$RH$	$-R \times 10^4$
8250	5.61	6.80	8250	5.85	7.10
9065	6.04	6.66	9065	6.35	7.01
9760	6.64	6.80	9760	6.77	6.94
			10090	7.06	7.00
$w_{290^\circ} = 126 \times 10^{-5} \Omega$			$w_{90^\circ} = 70 \times 10^{-5} \Omega$		

§ 8. Summary of the variation of the HALL coefficient for different metals. The results obtained in § 4—7 are collected in Tables XIII and XIV. For  $R$  is taken at each temperature the mean of the values <sup>1)</sup> for the different fields.

<sup>1)</sup> It has not been possible to determine the thickness of the plates with a greater accuracy than about 3%, which of course influences the absolute values of the HALL coefficients. This inexactitude, however, makes no difference as to the temperature coefficient of the HALL effect, the measurement of which has been the principal object of this investigation.

$T$	$Au_{pl}$	$Ag_{pl}$	$Cu_{pl}$	$Pd_{pl}$
290°K.	$7.24 \times 10^{-4}$	$8.00 \times 10^{-4}$	$4.92 \times 10^{-4}$	$6.75 \times 10^{-4}$
90°	7.61	8.21	5.56	6.99
77°	7.62	—	—	—

$T$	$Au_{pl}$	$Ag_{pl}$	$Cu_{pl}$	$Pd_{pl}$
290°K.	1	1	1	1
90°	1.05	1.025	1.13	1.035
77°	1.05	—	—	—

From these observations, therefore, the HALL coefficient for  $Au$ ,  $Ag$  and  $Pd$  is almost constant from ordinary temperature down to that of liquid air. A distinct increase is first observed on proceeding to hydrogen temperatures<sup>1)</sup>, which amounts to 25—35 % for Gold, Silver and Copper, and 100 % in the case of Palladium.

A. W. SMITH<sup>2)</sup> gives the following values for the ratio  $\frac{R_{83^\circ K}}{R_{293^\circ K}}$  for

$Au$	$Ag$	$Cu$	$Pd$
1.03	1.095	1.205	1.27

This gives agreement in the case of  $Au$ , but with  $Ag$  and  $Cu$ , and particularly with  $Pd$ , SMITH's results deviate considerably from mine. In the case of  $Cu$  and  $Ag$  the lack of agreement may perhaps be ascribed to the presence of impurity.

The relationship

$$R_0 = \frac{3\pi}{8N\epsilon}$$

deduced for the HALL effect by R. GANS<sup>3)</sup> has been utilised by

1) H. KAMERLINGH ONNES and BENGT BECKMAN, l. c.

2) A. W. SMITH, Phys. Rev. **30**. 1. 1910.

3) R. GANS, Ann. d. Phys. **20**. 293. 1906.

J. KOENIGSBERGER and J. WEISS<sup>1)</sup> to obtain the variation of the electron density ( $N$ ) from the temperature coefficient of the HALL effect. From this relation it should follow that the density of the electrons in  $Au$ ,  $Ag$ ,  $Cu$ ,  $Pd$  varies very slowly with the temperature, much more slowly than  $\sqrt{T}$ .

### III. Alloys.

§ 9. *Gold-silver*. The alloys investigated contained 2% of silver by volume.

TABLE XV.				
HALL effect for a gold alloy.				
$H$	$T = 290^\circ \text{ K.}$		$T = 90^\circ \text{ K.}$	
	$RH$	$-R \times 10^4$	$RH$	$-R \times 10^4$
8250	5.58	6.77	5.40	6.54
9065	6.18	6.82	6.01	6.63
9760	6.61	6.77	6.44	6.59
10270	6.94	6.76	6.86	6.67
0	$w_{290^\circ} = 3.81 \times 10^{-4} \Omega$		$w_{90^\circ} = 1.77 \times 10^{-4} \Omega$	

Hence the mean value of  $R$  is for

$$T = 290^\circ \text{ K.} \quad R = 6.78 \times 10^{-4}$$

$$90^\circ \quad R = 6.61$$

The hydrogen experiments gave<sup>2)</sup> for

$$T = 20.^\circ 3 \text{ K} \quad R = 6.69 \times 10^{-4}$$

$$T = 14.^\circ 5 \quad R = 6.48$$

Hence the HALL coefficient for this alloy is almost constant; on proceeding to low temperatures it begins to exhibit a slight *decrease*.

<sup>1)</sup> J. KOENIGSBERGER and J. WEISS, Ann. d. Phys. **35**. 1. 1911.

<sup>2)</sup> H. KAMERLINGH ONNES and BENGT BECKMAN, l. c.

**Physics.** — “On the HALL effect and the change in resistance in a magnetic field at low temperatures. V. Measurements on the HALL effect for alloys at the boiling point of hydrogen and at lower temperatures.” By H. KAMERLINGH ONNES and BENGT BECKMAN. Communication N<sup>o</sup>. 130<sup>c</sup> from the Physical Laboratory at Leiden.

### VI. Gold-silver alloys.

§ 16<sup>1)</sup>. In § 12 of Comm. N<sup>o</sup>. 129<sup>a</sup> observations on the HALL effect for an alloy of gold and silver ( $Au-Ag$ )<sub>I</sub> with 2 atom % of  $Ag$  are published. We now give the results of our measurements on two  $Au-Ag$  alloys, containing greater percentages of silver.

The alloy ( $Au-Ag$ )<sub>II</sub> contained 10,6 atom % of silver<sup>2)</sup>. The thickness of the plate was 0.049 mm. The HALL effect was measured at the temperatures  $T = 290^\circ$ ,  $20^\circ,3$  and  $14.5^\circ$  K.

We found:

$H$	$T = 290^\circ K.$		$T = 20^\circ,3 K.$		$T = 14.5^\circ K.$	
	$RH$	$-R \times 10^4$	$RH$	$-R \times 10^4$	$RH$	$-R \times 10^4$
8250	4.59	5.57	3.07	3.72	3.04	3.69
9360	5.47	5.61	3.47	3.71	3.52	3.76
10270	5.70	5.55	3.82	3.72	3.83	3.73
0	$w = 8.06 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 1.03$		$w = 4.58 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.585$		$w = 4.54 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.58$	

The alloy ( $Au-Ag$ )<sub>III</sub> contained 30 atom % of silver. The thickness of the plate was 0.078 mm.

We found:

<sup>1)</sup> The sections of this paper are numbered in continuation of those of Comm. N<sup>o</sup>. 129<sup>c</sup>. (Sept. '12).

<sup>2)</sup> The exact analysis being made now the composition is given in atom %.

T A B L E XVI.						
The HALL effect for $(Au-Ag)_{III}$ .						
$H$	$T = 290^\circ K$		$T = 20^\circ.3 K$		$T = 15^\circ K$	
	$RH$	$-R \times 10^4$	$RH$	$-R \times 10^4$	$RH$	$-R \times 10^4$
8250	4.62	5.60	3.00	3.64	3.12	3.78
9360	5.23	5.59	3.30	3.53	3.42	3.66
10270	5.67	5.53	3.73	3.63	3.81	3.71
0	$w = 9.47 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 1.015$		$w = 7.05 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.755$		$w = 7.02 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.75$	

The results of measurements on gold and on the three gold-silver alloys are brought together in the tables XVII and XVIII.

T A B L E XVII.				
The HALL coefficient for gold and gold-silver alloys.				
$T$	$Au_{pI}$	$(Au-Ag)_I$	$(Au-Ag)_{II}$	$(Au-Ag)_{III}$
$290^\circ K$	$7.2 \times 10^{-4}$	$6.8 \times 10^{-4}$	$5.6 \times 10^{-4}$	$5.6 \times 10^{-4}$
20.3	9.8	6.7	3.7	3.6
15.0	9.8	6.50	3.7	3.7

T A B L E XVIII.				
Change of the HALL coefficient $\frac{R_T}{R_{290^\circ K}}$ on cooling to and in the region of liquid hydrogen temperatures.				
$T$	$Au_{pI}$	$(Au-Ag)_I$	$(Au-Ag)_{II}$	$(Au-Ag)_{III}$
$290^\circ K.$	1	1	1	1
20.3	1.355	0.985	0.665	0.646
15	1.355	0.955	0.665	0.667

Thus,  $\frac{R_{T=20}}{R_{T=290}}$  diminishes by greater percentages of silver. For pure

gold  $R_{T=20.3} > R_{T=290}$ , but for alloys with more than 2 % of silver by volume  $R_{T=20.3} < R_{T=290}$ .

The curve that represents the relation between the HALL coefficient  $R_{T=20.3}$  and the percentages of silver is of a shape analogous to that representing the conductivity or the temperature coefficient of the resistance as a function of percentages of silver. The curve for  $R_{T=20.3}$  at first descends very rapidly for small admixtures of *Ag*; at higher concentrations it becomes flatter.

The HALL coefficient  $R_{T=20.3}$  is approximately a linear function of the quantity  $\frac{w_{T=20.3}}{w_{T=273}}$  for alloys with less than about 8 % by volume of *Ag*.

The HALL coefficient  $R_{T=290}$  diminishes too, though much more slowly than  $R_{T=20.3}$ , when the percentage of *Ag* increases.

**Physics.** — “*On the triple point of methane*”. By C. A. CROMMELIN.

Comm. N<sup>o</sup>. 131*b* from the physical Laboratory at Leiden.  
(Communicated by Prof. H. KAMERLINGH ONNES).

The measurements made by Prof. MATHIAS, Prof. KAMERLINGH ONNES and myself on the diameter for argon<sup>1)</sup> afforded an opportunity of determining the pressure and temperature of methane at its triple-point. For, when the cryostat was filled with liquid methane, and the pressure was reduced so as to give a temperature of about  $-183^{\circ}$  C. the methane was covered with a solid crust. A slight increase of the pressure caused the solid methane to spread itself in small pieces throughout the liquid. While these pieces were kept in constant motion through the liquid by means of the stirrer, the following triple point constants were observed:

$$t = -183.15 \text{ K.} \qquad p = 7.0 \text{ cm.}$$

On account of the manner in which these figures have been determined they must be considered to be very accurate.

As far as I am aware there has hitherto been only one other determination of these data — that of OLSZEWSKI<sup>2)</sup> — who found

$$t = -185.08 \text{ and } p = 8.0 \text{ cm.}$$

<sup>1)</sup> Comm. No. 131*a*.

<sup>2)</sup> K. OLSZEWSKI, C. R. 100, page 940, 1885.



**Physics.** — “*On the rectilinear diameter for argon.* By E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN. Comm. N°. 131a from the phys. Lab. at Leiden.

§ 1. *Introduction.* The present paper forms a continuation of the investigation of the diameter for substances of low critical temperature with which a beginning was made with oxygen.<sup>1)</sup> The importance of this and of similar investigations was indicated in the introduction to the Communication referred to, so that we need not discuss the point further here.

We chose argon for the present investigation since the isotherms for that gas had already been determined to within the neighbourhood of the critical point, while the critical point itself, the vapour pressures and even preliminary values of the densities of the coexisting vapour and liquid phases were already known<sup>2)</sup> the monatomic nature of the gas, moreover, will undoubtedly enhance the value of the results.

§ 2. *Apparatus.* The apparatus was essentially the same as that employed in the investigation of oxygen. The arrangement for compressing the argon and also the volumenometer have, however, undergone some modification since that time, so that it seemed desirable to take this opportunity of publishing a new diagram of the whole apparatus (Fig. 1).

The modifications of the volumenometer and of the auxiliary apparatus belonging to it have already been described in full detail<sup>3)</sup>.

The use of such a costly gas as pure argon necessitated, however, a completely new arrangement of the pressure connections. The copper tubes of which all the connections were made were chosen as narrow as possible so as to reduce the quantity of gas in the dead space to a minimum. The argon was contained in the steel cylinder A which was completely immersed in oil; so too were all the taps and coupling pieces which contained compressed gas.<sup>4)</sup>

Through the taps  $C_{16}$  and  $C_{13}$ , the gas passes to the spiral  $Sp$ ;

1) Proc. Febr. 1911. Comm. No. 117. C. R. 151, 213 and 477, 1910.

2) Proc. May 1910, Comm. No. 115, Proc. Dec. 1910, Comm. No. 118, C. A. CROMMELIN, Thesis for the doctorate, Leiden. 1910.

3) Proc. May 1911 Comm. No. 121a, Proc. Sept. 1912 Comm. No. 127c and W. J. DE HAAS, Thesis for the Doctorate, Leiden 1912, in which diagrams of the modified volumenometer are also given. Certain small errors in these diagrams make it desirable to publish a diagram here in which these errors are corrected.

4) Proc. June 1905 Comm. No. 94b. The value of this device for the detection of leaks has already been repeatedly emphasized

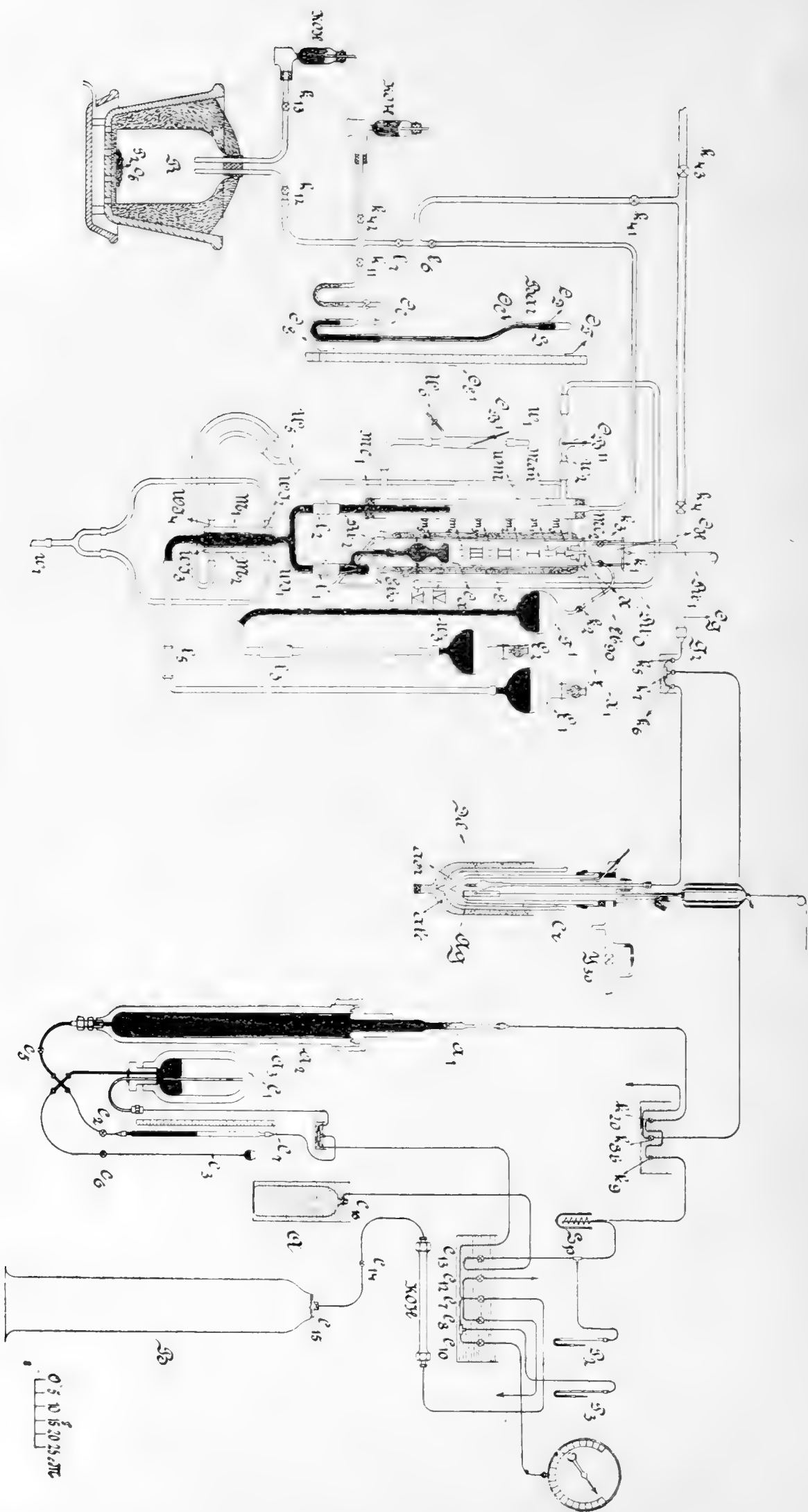


Fig. 1.

here the argon is dried by immersing this spiral in alcohol and cooling it down to its melting point by means of liquid air. Through  $k_9$  and  $k_{10}$  the gas then reaches the compression tube  $A$ , within the compression cylinder  $A_3$  <sup>1)</sup>. In this compression tube the mercury is forced by means of compressed air from the steel cylinder  $B$ ; by this the required amount of argon is compressed into the dilatometer on closing the tap  $k_9$  and opening  $k_7$  and  $k_6$ . This arrangement for compressing pure gases has already been fully described in previous Communications <sup>2)</sup>; moreover, its mode of operation is easily seen from the accompanying diagram.

Through the tap  $C_{12}$  it was possible to establish communication between the air compressor and our accurate closed hydrogen manometer <sup>3)</sup>, and by this means we were able during the actual measurements to obtain a few further determinations of the vapour pressure, which will be published shortly.

The cryostat  $C_1$  was the same as that used in the investigation of oxygen, the sole modification being the introduction of a different type of stirrer,  $A_9$ , provided with valves. <sup>4)</sup>.

As the appendix of the dilatometer formerly used was found to be too narrow, another dilatometer  $Dil$ , very accurately calibrated, was employed with an appendix sufficiently wide to allow of the suitable measurement of the small volume of the liquid coexisting with the vapour.

A GAEBE vacuum pump was used, and we found it of the greatest utility, particularly during the actual measurements, in ensuring the continued absence of leaks.

Two platinum resistance thermometers were introduced into the cryostat to serve for the regulation and measurement of the temperature.

The argon used for the present measurements was taken from the same supply as that employed in the previous investigations already quoted. The impurity in this argon is certainly less than 0.1 % <sup>5)</sup>.

§ 3. *Experiments.* We may now give a short description of the sequence of operations involved in the measurements :

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<sup>1)</sup> At the cylinder  $A$  is connected the glass manometer  $P_2$  for high pressures and of small volume, especially constructed for the use of such cylinders as reservoirs for the rare gases.

<sup>2)</sup> Proc. April 1901 Comm. No. 69, Proc. March 1907 Comm. 97a.

<sup>3)</sup> April 1902 Comm. no. 78, Proc. March 1907 Comm. no. 97a.

<sup>4)</sup> Proc. June 1911. Comm. no. 123.

<sup>5)</sup> For a detailed description of the preparation and of the analysis of this argon see C. A. CROMMELIN, Thesis for the Doctorate, Leiden, 1910.

1. All the apparatus and connections were reduced to a high vacuum and then washed out with argon.
2. The cryostat was filled with the liquid gas desired ( $O_2$ ,  $CH_4$ , or  $C_2H_4$ ).
3. The argon was admitted to the compression tube  $A_2$  and then pumped into the dilatometer.
4. The argon meniscus was adjusted to the upper part of the stem of the dilatometer, and the tap  $k_3$  was closed.
5. When the temperature is constant the position of the argon meniscus is read, the temperature is measured, and also when required, the pressure registered by the hydrogen manometer.
6. By reducing the pressure in the cryostat transition is made to a lower temperature, the same measurements are repeated; a lower temperature is then installed and so on until the meniscus has sunk below the subdivided portion of the stem.
7. Sufficient argon is then allowed to escape into the volumenometer to bring the meniscus to the lower part of the appendix below the dilatometer; the temperature, pressure and volume of the escaped gas are measured.
8. The measurements of  $5^\circ$  and  $6^\circ$  are repeated in the reversed order of temperature until the meniscus reaches the upper part of the appendix.
9. The argon still remaining in the dilatometer is transferred to the volumenometer, and the measurements of  $7^\circ$  are repeated.

It is clear that these measurements yielded the data requisite for the calculation of the liquid and vapour densities at all the experimental temperatures. To these calculations we shall return in the succeeding section.

The dimensions of the dilatometer were so calculated that one could finish off the temperature range for any particular substance by successive measurements; in this way only two measurements with the volumenometer were required to give both the liquid and vapour densities.

§ 4. *Calculations.* In many respects the calculations were made in the same way as those of Comm. No. 117. It was of great advantage to us that so many data are already available for argon, and that we could already make use of the reduced equation of state, VII. A. 3.<sup>1)</sup> We shall, however, here give a short summary of the method adopted in the calculations.

Working from the very accurate calibration of the dilatometer,

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<sup>1)</sup> Proc. June 1912, Comm. no. 128.

the *liquid volumes* were first calculated directly from the positions of the meniscus top in the stem and in the appendix, without applying any correction. To the numbers so obtained the following corrections were then applied:

1. A fairly large correction for the diminution of the volume at low temperature, seeing that the calibration of the dilatometer had been reduced to  $+ 20^{\circ}$  C.; the correction was obtained by means of a formula from a former Communication <sup>1)</sup>).

2. A correction for the increase of volume due to the pressure. For this correction, which was so small as to be negligible in almost every case, approximate values were calculated from data contained in two previous Communications <sup>2)</sup>).

3. A correction for the volume of the argon meniscus. KELVIN'S graphical method <sup>3)</sup> was employed for the evaluation of this by no means negligible correction. To obtain the volume of the menisci it was usually sufficient for our purpose to regard the surface of the liquid as half of an oblate ellipsoid of revolution. Only at the higher temperatures was it necessary to apply GULDIN'S theorem to the KELVIN diagram in order to determine the body of revolution.

<sup>1)</sup> Proc. Sept. 1906, Comm. no. 95b.

<sup>2)</sup> Proc. April 1902, Comm. no. 78, Proc. March 1907, Comm. no. 97a.

<sup>3)</sup> The capillary constant for argon and its variation with temperature must be known for the construction of these diagrams. Now BALY and DONNAN (Journ. of the Chem. Soc. Trans. 81. 907. 1902) have determined capillary constants for liquid argon but only between  $- 189^{\circ}$  C. and  $- 183^{\circ}$  C. so that the question now arose as to how to interpolate in the most rational manner possible from  $- 183^{\circ}$  C. to the critical temperature. A comparison between the results giving

the reduced capillary constant  $\frac{\psi_{\sigma}}{T_k^{1/3} p_k^{2/3}}$  (see J. D. VAN DER WAALS, Cont. I. p.

176) as a function of the reduced temperature by BALY and DONNAN (l.c.), for argon, by DE VRIES (Zittingsversl. Febr. 1893, Comm. no. 6, and Thesis for the doctorate, Leiden 1893) for ether, by VERSCHAFFELT (Zittingsversl. Juni 1895, Comm. no. 18) for carbon dioxide and nitrous oxide was fruitless, seeing that the last three correspond well, while argon deviates strongly from them. A suitable rational method is given by the assumption of the validity of the EÖTVÖS formula (Ann. d. Phys. und Chem. 27 (1886) p. 448) according to which the quantity

$\psi_{\sigma} \left( \frac{M}{\rho_{\text{liq}}} \right)^{2/3}$  is a linear function of the temperature. According to BALY and DONNAN

we get for argon  $\psi_{\sigma} \left( \frac{M}{\rho_{\text{liq}}} \right)^{2/3} = 2.020 (145.44 - T)$ ; from this formula our esti-

mates have been made except that for the highest temperature,  $\pm - 125^{\circ}$  C., at which one is so close to the critical temperature that the EÖTVÖS formula no longer holds, and for which interpolation was resorted to in correspondence with the curves given by other substances.

Having thus calculated all the liquid volumes, we were able, taking the first two of the above corrections into account, to obtain *the volumes of the saturated vapour*. In this it was assumed that the temperature of the bath extended to a distance of 2 cms. above the surface of the liquid.

The following method was adopted of *reducing the gaseous argon* in the glass and steel capillaries from the point of the capillary just mentioned up to the tap  $k_6$  to terms of the normal volume. The portion of the glass capillary within the cryostat was divided into different parts for each of which the mean temperature was known from previous papers<sup>1)</sup>. The temperatures of the part of the glass capillary outside the cryostat and of the steel capillary up to the tap  $k_6$  were obtained from thermometers during the measurements. The volumes of all these portions were known from the calibrations and the pressures from the vapour pressures already published<sup>2)</sup> together with those added by the present measurements.

In order now to obtain the normal volume of all these portions at different temperatures we again make use of the modified series

$$pv_N = A_N \{1 + B^{(p)} p + C^{(p)} p^2 + \dots\}$$

Since  $v_N = \frac{V}{N}$  and  $A_N = A_{NO^\circ C.} (1 + \alpha_A t)$ , it follows that

$$N = \frac{pV}{A_{NO^\circ C.} (1 + \alpha_A t) [1 + B^{(p)} p + C^{(p)} p^2]} \quad ^3)$$

The virial coefficients necessary for the employment of this equation were taken from the equation VII. A. 3. In all these calculations the coefficient  $C^{(p)}$  could be neglected.

We may again refer to previous papers<sup>4)</sup> for the corrections which have to be applied to the volumetric determinations.

For the normal specific mass of argon we used the value given by RAMSAY and TRAVERS<sup>5)</sup> 0.001782.

1) C. BRAAK, Thesis for the doctorate, Leiden. 1908. p. 16.

2) Proc. May 1910, Comm. N<sup>o</sup>. 115.

3) In these formulae  $p$  is the pressure in atmospheres,  $v_N$  the volume expressed in terms of the normal volume as unit,  $N$  the normal volume,  $V$  the actual experimental volume and  $\alpha_A$ , the coefficient of expansion in the AVOGADRO state, 0.0036618. For the notation see also Suppl. No. 23.

4) Proc. May 1911, Comm N<sup>o</sup>. 121a. Proc. Sept. 1912 Comm. N<sup>o</sup>. 127c and W. J. DE HAAS. Thesis for the doctorate, 1912.

5) W. RAMSAY and M. W. TRAVERS, Proc. R. S. 67. 329. 1900.

We may further state that at the lowest three temperatures the vapour densities were not measured but calculated; in view of the degree of accuracy desired this is quite permissible. The calculation was made by means of the above series in which, however,  $C^{(v)}$  is now no longer negligible. *(To be continued).*

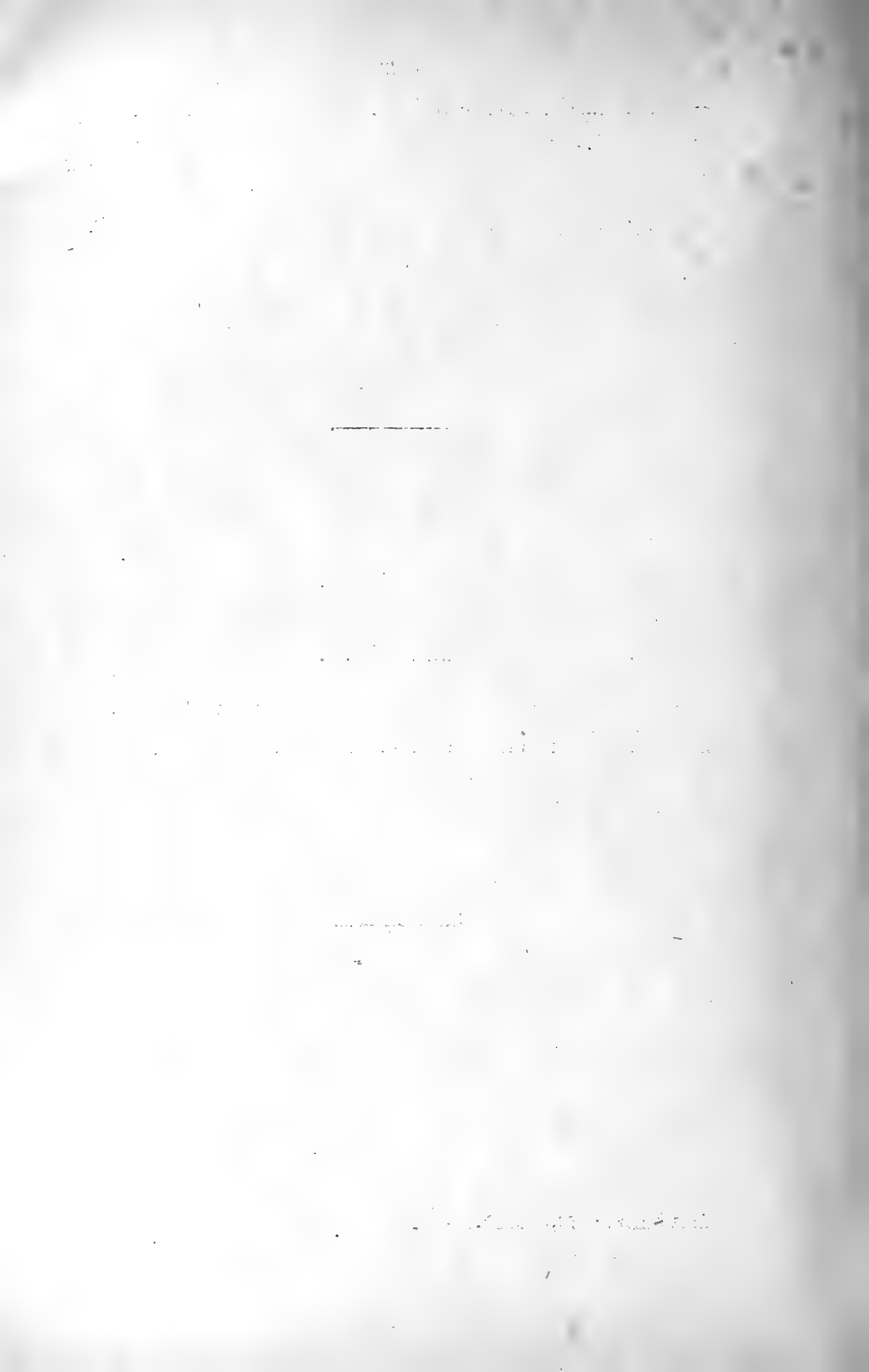
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ERRATUM.

In the Proceedings of the meeting of September 28, 1912.  
p. 415 l. 10 from the top: for 0.507834 read 0.057834.

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(November 28, 1912).





# KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

## PROCEEDINGS OF THE MEETING of Saturday November 30, 1912.

*President:* Prof. D. J. KORTEWEG.

*Secretary:* Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 30 November 1912, Dl. XXI).

### C O N T E N T S.

- A. SMITS and H. L. DE LEEUW: "The system tin". (Communicated by Prof. A. F. HOLLEMAN), p. 676.
- A. SMITS and S. C. BOKHORST: "The phenomenon of double melting for fats". (Communicated by Prof. A. F. HOLLEMAN), p. 681.
- A. SMITS and A. KETTNER: "On the system ammonium sulphocyanate thioureaum water". (Communicated by Prof. A. F. HOLLEMAN), p. 683.
- C. VAN WISSELINGH: "On the demonstration of carotinoids in plants. Second communication: Behaviour of carotincids with regard to reagents and solvents", p. 686. Third communication: "The leaf of *Urtica dioica* L., the flower of *Dendrobium thyrsiflorum* Rehb. fil. and *Haematococcus pluvialis* Flot". (Communicated by Prof. J. W. MOLL), p. 693.
- F. A. H. SCHREINEMAKERS: "Equilibria in ternary systems" I, p. 700.
- J. C. SCHOUTE: "Dichotomy and lateral branching in the Pteropsida", p. 710.
- Hk. DE VRIES: "On loci, congruences and focal systems deduced from a twisted cubic and a twisted biquadratic curve" II, p. 712.
- L. J. J. MUSKENS: "The posterior longitudinal fascicle, and the manege movement". (Communicated by Prof. C. WINKLER), p. 727. (With one table).
- H. A. BROUWER: "On the formation of primary parallel structure in lujaurites" (Communicated by Prof. MOLENGRAAFF), p. 734.
- I. J. H. M. KLESSSENS: "Form and function of the trunkdermatome tested by the strychnine-segmentzones". (Communicated by Prof. WINKLER), p. 740. (With one plate).
- II. J. WATERMAN: "Action of hydrogenious, boric acid, copper, manganese, zinc and rubidium on the metabolism of *Aspergillus niger*". (Communicated by Prof. M. W. BEIJERINCK), p. 753. (With one table).
- ERNESTINE DE NEGRI and C. W. G. MIEREMET: "On a micro-organism grown in two cases of uncomplicated Malignant Granuloma". (Communicated by Prof. C. H. H. SPRONCK), p. 765. (With one plate).
- J. F. SIRKS: "Measurements on the ultraviolet magnetic rotation in gases". (Communicated by Prof. H. KAMERLINGH ONNES), p. 773.

**Physics.** "*The system tin*". By Prof. A. SMITS and Dr. H. L. DE LEEUW.  
(Communicated by Prof. A. F. HOLLEMAN).

(Communicated of the meeting of October 26, 1912).

As is known when molten tin is cooled down, the tetragonal modification deposits under ordinary circumstances, which form was first described by MILLER<sup>1)</sup> in 1843. This form shows a point of transition at 18<sup>°</sup>), below which the gray tin is the stable modification.

In the years 1880 and 1881 TRECHMANN<sup>3)</sup> and FOULLON<sup>4)</sup> discovered moreover a third modification, viz. a rhombic one, which can be formed when molten tin is exceedingly slowly cooled down, and which is *brittle*.

It was now natural to assume that this form of tin forms at higher temperature from the tetragonal modification, for it had been known for a long time that tin heated to about 200<sup>°</sup> becomes *brittle*, and that in England this circumstance has been profitably used to obtain the so-called *corn tin* or *grain tin*. In this process tin is heated to some degrees under the melting-point, after which it is dropped from a great height on a stone plate, on which the metal breaks up into pieces resembling basalt. The above-mentioned supposition was further supported by observations by KALISCHER<sup>5)</sup>, in which it appeared that when tin is heated to about 200<sup>°</sup>, the aspect changes, and the metal assumes the appearance of *moiré métallique*.

As SCHAUM<sup>6)</sup> already observed these experimental data make the existence of a point of transition at about 200<sup>°</sup> very probable, and as the spec. gravity of the tetragonal and rhombic modification, which amount to 7,25 resp. 6,55 at 15<sup>°</sup> differ pretty much, it seemed the natural course to take to try and find this point of transition by a dilatometrical way. COHEN and GOLDSCHMIDT's<sup>7)</sup> experiments with an oil-dilatometer, however, (in which no difficulty was experienced from any generation of gas) did not furnish the least indication for the existence of a point of transition, for the expansion, represented as function of the temperature, appeared to be a perfectly straight line from 175<sup>°</sup> to 210<sup>°</sup>. Though these experiments had yielded a negative result, already a year before WERIGIN, LEWKOJEFF and TAMMANN<sup>8)</sup> had

<sup>1)</sup> Phil. Mag. (3) 22, 263 (1834).

<sup>2)</sup> COHEN-VAN EYK, Z. f. phys. Chem.

<sup>3)</sup> The mineralogical magazine and Journal of the Mining Soc. 3, 186 (1880).

<sup>4)</sup> Verh. der k. k. geologischen Reichsanstalt 1881, 237.

Jahrb. der k. k. geologischen Reichsanstalt 1884, 367.

<sup>5)</sup> B.B. 15, 722 (1113).

<sup>6)</sup> Lieb. Ann. 308, 18 (1899).

<sup>7)</sup> Z. f. phys. chem. 50, (1904).

<sup>8)</sup> Drud. Ann. 10. 647 (1903).

found indications which seemed to point to a point of transition in the neighbourhood of  $200^{\circ}$  in a determination of the velocity of effluxion of some metals, among which tin, at different temperatures.

Their results were the following :

temperature	velocity of effluxion
162.8	$0.6 \pm 0.3$
173.4	$1.7 \pm 0.3$
183.8	$3.9 \pm 0$
193.5	$8.2 \pm 0.1$
203.8	$12.1 \pm 2.1$
204.0	$3.2 \pm 0.3$
214.8	$4.1 \pm 0.5$
224.6	$10.5 \pm 0.4$
235.7	112.3

The above-mentioned investigators make the following remarks about this result :

“Von Interesse sind noch die beim *Zinn* bei  $200^{\circ}$  deutlich auftretenden Abnormalitäten in der Temperaturabhängigkeit der Ausflussgeschwindigkeiten. Beim *Zinn* fällt bei jener Temperatur plötzlich die Ausflussgeschwindigkeit. Der Grund hierfür kann nur in der Bildung einer neuen Kristallart, also im Auftreten eines Umwandlungspunktes gesucht werden. Von *Zinn* ist bekannt, dass es bei  $200^{\circ}$  spröde und pulverisierbar wird. Genauer sind diese Umwandlungspunkte bisher nicht untersucht worden.”

Why in reference to these experiments COHEN and GOLDSCHMIDT give  $195^{\circ}$  for the point of transition in question in the “*Chemisch Weekblad*”, and  $170^{\circ}$  in the *Zeitschr. f. phys. chem.* is quite unaccountable. Their assertion : “Bringt man die in Tabelle 4 (the above table) gefundenen Werte in Zeichnung, so entstehen zwei Kurven, welche sich bei etwa  $170^{\circ}$  schneiden, somit auf einen Umwandlungspunkt bei dieser Temperatur hinweisen”, is decidedly erroneous, and proves that they have not understood the significance of this curve.

In view of the fact that the experiments on the velocity of effluxion render a point of transition at more than  $200^{\circ}$  very probable, it was very desirable to get certainty on this point by another way, the more so as the experiments about the velocity of effluxion refer

to pressures of **500** kg. per cm<sup>2</sup>. There was therefore every reason to rejoice that Mr. DEGENS, when revising his Thesis for the Doctorate: "Legeeringen van tin en lood" (Alloys of tin and lead) wanted to make another attempt to find the expected transition between tetragonal and rhombic tin in a dilatometric way, though his predecessors had only obtained negative results.

As Mr. DEGENS found it impossible to obtain reliable results with paraffin oil, which had been used as dilatometric liquid by COHEN and GOLDSCHMIDT, in consequence of the generation of gas, however slight, one of us (SMITS) advised Mr. DEGENS to use an air-dilatometer with a twice bent capillary. To prevent any injurious decomposition of the dilatometric liquid, mercury was used by Mr. DEGENS, to include the air in the dilatometer, although in this way there was, of course, a possibility that during the experiment, especially when it had to be continued for a long time, appreciable quantities of gaseous mercury could be absorbed by the tin. Mr. DEGENS, however, expressly states that "it was never observed that the metal was attacked by mercury vapours".

By the aid of this air-dilatometer Mr. DEGENS really found an indication about the existence of a point of transition, viz. at **161°**.

Since we have been occupied with the tin-problem, we have begun to mistrust this temperature, because different phenomena led us to expect a point of transition at  $\pm 200^\circ$ . And as it seemed very desirable in connection with the already partially published investigation about the system tin, to know the exact situation of the point of transition between tetragonal and rhombic tin, an investigation was undertaken also by us to determine this point dilatometrically.

When we repeated Mr. DEGENS' experiments we found first of all that by this way of procedure a point of transition can really be demonstrated, but that in successive experiments this point of transition descended. This pointed to an absorption of gaseous mercury by the tin during the experiment. On investigation of the tin used it appeared clearly that the tin contained appreciable quantities of mercury, which to our great regret condemned Mr. DEGENS' method. We regretted deeply that we had to come to this conclusion, particularly because Dr. DEGENS was known to one of us (SMITS) as a man full of enthusiasm for his work, who carried out his investigations with great experimental skill, in the conviction of having left no means untried to test the validity of his results. In this case, however, he has been mistaken.

In order to take the experiment in such a way that the results

obtained were entirely reliable, we turned back to the ordinary dilatometer, and tried to attain by means of the oil of the vacuum pump of GOEDE, which seemed to be very suitable as dilatometric liquid, that no generation of gas took place at temperatures up to the melting-point of tin. By thoroughly boiling the oil in the vacuum of the pump, by then allowing it to flow into the dilatometer vessel, and afterwards heating the whole  $20^{\circ}$  above the melting-point of tin we managed to prevent any generation of gas even above the melting-point of tin <sup>1)</sup>.

With the dilatometer filled in this way curves of expansion and of contraction were determined as accurately as possible by putting the apparatus in a thermostat with oil resp. a molten mixture of  $\text{KNO}_3$  and  $\text{NaNO}_2$ , by raising the temperature every time  $10^{\circ}$ , resp. lowering it, and by then reading the position of the oil level after 15 minutes. Though the obtained lines have not appeared to be perfectly straight, as COHEN and GOLDSCHMIDT found, yet no indication of a point of transition was to be detected. As according to Mr. DEGENS' method, by the same procedure a point of transition *was* found for tin containing mercury the mercury seemed to be a positive catalyst for the conversion in the point of transition. In connection with this we proceeded to the determination of the transition point of tin to which small quantities of mercury had been added.

In this it was not only found that for every mixture very clearly a transition point occurred, but also that the transition point was greatly lowered by mercury, which is in accordance with the slight heat of transition.

We found :

	at. % Hg of the mixture	transition temperature
1	0.12	$173^{\circ}$
2	0.22	$151^{\circ}$
3	0.34	$133^{\circ}$
4	0.49	$133^{\circ}$

The third and fourth determinations point to the existence of three-phase equilibrium, which is also in harmony with this that the transition

<sup>1)</sup> Not to lose the oil during the heating up to this high temperature, the upper end of the capillary was provided with a wider vessel,

points **3** and **4** do not lie on the line drawn through **1** and **2** <sup>1)</sup>.

If we use the first two observations to extrapolate to the composition 0 atom % Hg, which is, of course, a rather inaccurate method, we find 200°,5 for the transition point of pure tin.

At all events it appeared from this that the transition point of pure tin must lie in the neighbourhood of 200°, and as it had appeared from the preceding experiments that the conversion in the transition points of mixtures containing Hg is attended with a distinct though small diminution of volume, it must also be possible to find the transition point for perfectly pure tin by dilatometrical way.

It was clear that the conversion in pure tin proceeds slowly, and that at every temperature we should have to wait long to attain reliable results.

When the thermostat, in which the dilatometer which contained 250 gr. of tin, was placed, was first regulated at 240°, so that the tin melted, and when then comparatively rapidly the thermostat was brought to 190°, it appeared that after the dilatometer had assumed the temperature of 190°, no change of volume worth mentioning took place even after 24 hours, from which it was inferred that on solidification exclusively the tetragonal modification had been formed, and that therefore the tin had solidified at the metastable point of solidification.

In agreement with this experiment it appeared that when the bath was regulated at 206°, and also the tin had assumed this temperature, an increase of volume took place, which could not practically be considered as completed until after 48 hours. If then the thermostat was again put at 190°, a diminution of the volume set in again at constant temperature.

This phenomenon, which points to the conversion :



shed a great deal of light on the fact of tin becoming brittle at about 200°, on the preparation of corn tin, and also on KALISCHER's observation, particularly because it is very probable that the above conversion proceeds most slowly in pure material.

It further appeared from these experiments, just as from those made with tin containing mercury, that the difference in specific gravity between the tetragonal and the rhombic modification is much smaller at  $\pm 200^\circ$  than at the ordinary temperature, as the variation of volume found, which, it is true, had probably not yet reached its

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<sup>1)</sup> This investigation is being continued to get to know more about the system tin-mercury.

maximum value, amounted only to about 0,3 cm<sup>3</sup>., which variation of volume corresponded with a displacement of the oil-level of  $\pm 6$  cm. in the capillary.

With a purpose of determining the accurate situation of the transition point the experiments described above were repeated several times, which resulted in a final determination of the transition point, which had been sought so long in vain, at  $\pm 202,8^\circ$ , for at this temperature no variation of volume had taken place even after four days, whereas below it a diminution of volume and above it an increase of volume was observed. The inaccurate extrapolation which was mentioned before, and which gave  $200,5^\circ$  for the transition temperature, yielded, therefore, a result which was pretty near the truth.

As we have always got the impression in this investigation that even on slow cooling of pure liquid tin exclusively or almost exclusively the tetragonal modification, which is metastable above  $203^\circ$ , is formed, and that even with pretty slow heating of the tetragonal form the conversion to the rhombic modification fails to appear, it seemed pretty certain that only the metastable unary melting-point of tin was known. To find the stable unary melting-point the curve of heating was determined of tin which had been heated for 48 hours at  $220^\circ$  in a thermostat. The result yielded by this investigation and the particularities of the pseudo system derived from it will be communicated in a following paper.

*Anorg. laboratorium of the University.*

*Amsterdam, Oct. 23, 1912.*

**Chemistry.** — “*The phenomenon of double melting for fats*”. By Prof. A. SMITS and S. C. BOKHORST. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of October 26, 1912).

GUTH <sup>1)</sup>, who has been extensively occupied with the preparation of simple and mixed glycerin esters of fatty acids, has observed the phenomenon of *double melting* for several of these fats. Thus we hear about tristearin that the crystallised tristearin has only one melting-point at  $71^\circ.5$ , whereas the tristearin that has first been melted, then cooled in a capillary, and then solidified, first melts at  $55^\circ$  on supply of heat, then solidifies again, and then melts again at  $71^\circ.5$  on further supply of heat. On the ground of these phenomena GUTH has come to the result that the melted and rapidly

<sup>1)</sup> Z. f. Biol. 44, 78 (1902).

cooled mass has not yet crystallised, and is therefore in a glassy metastable state. On supply of heat the metastable state would pass into the stable one, in which so much heat is liberated that small quantities are thereby completely melted, which later solidify again, but which melt again when the melting point has been reached for the second time on supply of heat.

KREIS and HAFNER <sup>1)</sup> have repeated GUTH's experiments and found them perfectly confirmed, but what rouses our great astonishment is this that they entirely concur in GUTH's view of the matter.

Without entering into GUTH's explanation, which is, putting it mildly, very improbable, we will state here very briefly what has been the result of an investigation which we have carried out with the purest *tristearin* of KAHLBAUM.

It is clear from what precedes that in GUTH's opinion the temperature of  $55^{\circ}$  cannot be called a melting point of tristearin. Our experiment, however, has shown that GUTH has stated the truth, in spite of himself, and that we have, indeed, to do here with two melting-points. It has namely appeared that the observed peculiar phenomenon is caused by the existence of two different crystallised modifications of tristearin, of which the metastable one appears most readily. The velocity of crystallisation of the stable form is still very small, even a few degrees below the point of solidification of the metastable form, and much smaller than that of the metastable modification. Hence when the liquid is cooled down to below the point of solidification of the metastable form, the latter is always made to crystallise.

*If the liquid is kept for some time at a temperature between the two melting-points, the stable form crystallises, but with a very slight velocity.*

If we start from the metastable modification obtained by comparatively rapid cooling of the liquid, and if this metastable modification is placed in a bath the temperature of which rises slowly, the metastable unary melting-point appears at  $54^{\circ}.5$ ; if the temperature of the bath is carried up to  $63^{\circ}$ , and if this temperature is kept constant for some time, crystallisation sets in slowly, and only after 2 or 3 hours everything has become solid and has passed into the stable modification. If the temperature of the bath is made to rise still further, the stable unary melting point occurs at  $70^{\circ}.8$ . The phenomena described just now have also been studied under the microscope, in which our views were perfectly confirmed in all respects.

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<sup>1)</sup> B. B. 36, 1123.



In conclusion we will still remark here that the system *tristearin*, which according to our investigation exhibits the phenomenon of *allotropy*, and is probably monotropic, has also furnished a confirmation for the theory of allotropy, as it has appeared here again that the *solid phases are states of internal equilibrium*. Particularly for the metastable modification it could be clearly demonstrated that the solid substance which has assumed equilibrium at lower temperature, melted already below the metastable unary melting-point in case of rapid heating.

Hence it follows from what precedes that we have to assume two kinds of molecules  $\alpha$  and  $\beta$  for the system *tristearin*, and that the differences between the two crystallised states are owing to the difference in situation of the internal equilibria.

That the phenomenon of double melting observed for other fats, will have to be accounted for in the same way, is more than probable.

*Anorg. Chem. Laboratory of the University.*

*Amsterdam, Oct. 25.*

**Chemistry.** — “*On the system ammonium sulphocyanate-thiourea-water.*” By Prof. A. SMITS and A. KETTNER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of October 26, 1912).

A recently published paper by ATKINS and WERNER<sup>1)</sup> induces us briefly to communicate already now the results of an investigation which is not yet quite completed.

The pseudo binary system  $\text{NH}_4\text{CNS} - \text{CS}(\text{NH}_2)_2$  was examined. The melting-point figure found for this system (fig. 1) pointed with great probability, to the existence of a compound  $\text{NH}_4\text{CNS} \cdot 4 \text{CS}(\text{NH}_2)_2$  because the curves of cooling on the right of this concentration did not give a single indication for a eutectic point at  $\pm 105^\circ$ , whereas this *was* the case for mixtures on the leftside of this concentration. ATKINS and WERNER are, however of opinion that the compound  $\text{NH}_4\text{CNS} \cdot 3 \text{CS}(\text{NH}_2)_2$  follows from the melting-point lines found by them, which show a close resemblance to ours<sup>2)</sup>.

To get perfect certainty about the existence of the compound  $1 \cdot 4$ ,

<sup>1)</sup> Journ. Chem. Soc 101, 1167 (1912).

<sup>2)</sup> On account of the rapid conversion of  $\text{CS}(\text{NH}_2)_2$  at high temperature, the mixtures with more than 70%  $\text{CS}(\text{NH}_2)_2$  had to be investigated by SOCH's capillary method.

the study of the ternary system  $\text{NH}_4\text{CNS} - \text{CS}(\text{NH}_2)_2 - \text{H}_2\text{O}$  was taken in hand after the melting-point diagram had been determined, in which a method of analysis was worked out which enabled us

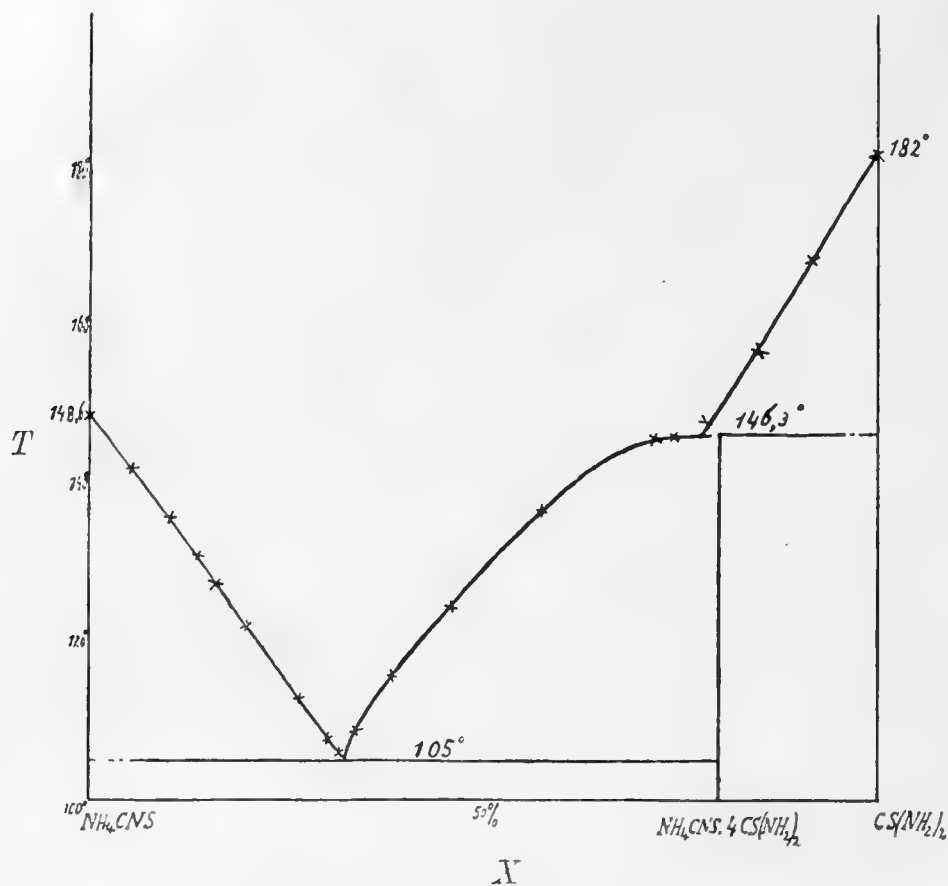


Fig. 1.

quantitatively to determine the ammonium sulpho-cyanate and the thiourem by the side of each other with sufficient accuracy.

The solubility-isotherms found at  $25^\circ$  and the investigation of the coexisting solid phases, in which the residu-method was applied for the determination of the binary compound (see fig. 2) afforded a proof for the validity of the conclusion drawn from the melting-point figure, so that the existence of the compound 1.4 may now be considered as conclusively proved.

Moreover the knowledge of the peculiar situation of the solubility isotherms led us to a simple explanation of the method of preparation of thiourem from ammonium sulphocyanate according to REYNOLDS and WERNER<sup>1)</sup>, which method had been unaccountable up to now.

The process of preparation is as follows: ammonium sulphocyanate is heated for some time up to  $160^\circ$ , then the liquid is poured into

<sup>1)</sup> Journal Chem. Soc. 83, 1 (1903).

cold water, and then the solid substance obtained by evaporation is recrystallised.

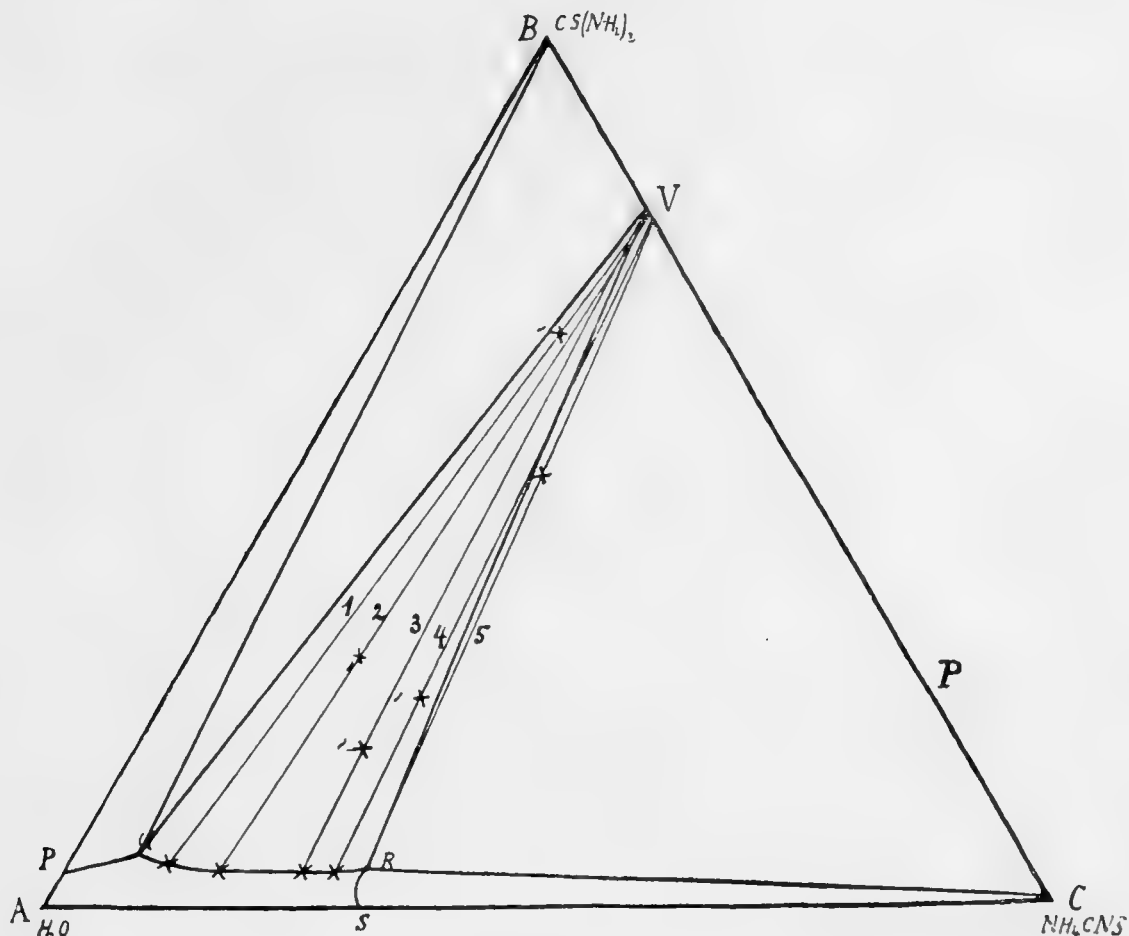


Fig. 2.

According to FINDLAY'S<sup>1)</sup> experiments, and also according to ours the internal liquid equilibrium that sets in when ammonium sulphocyanate is heated up to  $160^{\circ}$  for some time, has the following composition 75%  $\text{NH}_4\text{CNS}$  and 25%  $\text{CS}(\text{NH}_2)_2$ . When the liquid is poured into cold water, this state is fixed. If we suppose that everything is solved at  $25^{\circ}$ , the obtained state lies in our figure on the line that joins the points  $P$  and  $A$ , and in the unsaturate region. If we now begin to make the liquid evaporate, the isotherm of the compound  $\text{NH}_4\text{CNS} \cdot 4\text{CS}(\text{NH}_2)_2$  will be passed, i. e. we may enter the region which is supersaturate of the compound 1,4 indicated by the point  $V$ , so that the latter deposits. If we now separate the solid substance from the mother liquor and if we solve the compound  $V$  in a new quantity of water, the obtained liquid will again lie in the unsaturate region, but now on the line that connects point  $V$  with  $A$ . This joining line accidentally does not cut the isotherm of the compound  $V$ , but that of the thiouream ( $B$ ), so that on evaporation of the solution, not the compound  $V$ , but thiouream will

<sup>1)</sup> Journal Chem. Soc. 85, 403 (1904).

deposit. It is clear that to obtain thiourea from the compound  $V$  it is not even necessary to dissolve the latter first entirely. It already suffices to bring the compound in contact with water, because the pure saturated solution of  $V$  is metastable, and will deposit thiourea specially on seeding with a crystal of this substance, which conversion continues till the compound has quite vanished.

With regard to the exact relation between the pseudo-binary and the unary  $T$ , x-figure of the system  $\text{NH}_4\text{NCS} - \text{CS}(\text{NH}_2)_2$  we may state that it is being investigated, and that we hope that we shall soon be able to give it with perfect certainty.<sup>1)</sup>

*Anorg. Chem. Laboratory of the University.*

*Amsterdam, Oct. 25, 1912.*

**Botany.** — “*On the demonstration of carotinoids in plants. Second communication: Behaviour of carotinoids with regard to reagents and solvents.*” By Prof. C. VAN WISSELINGH. (Communicated by Prof. J. W. MOLL).

(Communicated in the meeting of October 26, 1912).

The reagents by means of which coloration is brought about in carotinoids are the following: concentrated sulphuric, sulphurous and concentrated nitric acids, bromine water, concentrated hydrochloric acid with a little phenol or thymol, and iodine in potassium iodide or chloralhydrate solution. All these reagents cause blue coloration, except the iodine reagents which generally produce a green colour.

In this paper the use of sulphuric acid, bromine water and iodine in potassium iodide solution will be dealt with as well as two new reagents for carotinoids, namely, concentrated solutions of antimony trichloride and of zinc chloride both in 25 % hydrochloric acid. Solvents as well as reagents can also be successfully used in the microscopic investigation of carotinoids, and they also are dealt with in this paper.

#### *Sulphuric acid.*

T. TAMMES<sup>2)</sup> in her investigation of carotin used concentrated

<sup>1)</sup> This relation is probably pretty complicated, because different crystallized modifications exist of both pseudo-components. This was already known of  $\text{NH}_4\text{NCS}$ , but for  $\text{CS}(\text{NH}_2)_2$  it was revealed for the first time by this investigation.

<sup>2)</sup> T. TAMMES, Ueber die Verbreitung des Carotins im Pflanzenreiche, *Flora* 1900, 87. Bd. 2. Heft, p. 213.

sulphuric acid, concentrated hydrochloric acid containing a little phenol, concentrated nitric acid and bromine water, and she completely dried the preparations over sulphuric acid in a dessicator. She maintains that with sulphuric acid and hydrochloric acid containing phenol, this is absolutely necessary and is to be recommended in the case of nitric acid and of bromine water. TAMMES says that when the preparations are even slightly moist, the reaction sometimes does not take place, and she attributes this, especially in the case of sulphuric acid, to the presence of traces of water. When investigating the crystals which have been separated out in the cells and tissues as also when working with plants and parts of plants, which have not yet been treated with other reagents, TAMMES prescribes the careful drying of the preparations. KOHL<sup>1)</sup> completely agrees with this. My impression is, however, that he does not support his opinion by experiments. G. and F. TOBLER<sup>2)</sup> state moreover that the assertion that the reaction with sulphuric acid succeeds only with anhydrous objects, is not correct.

With respect to TAMMES' method of procedure it must be remarked that a thorough drying is not a suitable method for obtaining beautiful preparations, and there is no theoretical explanation why this drying is necessary, for concentrated nitric acid contains 50 % water, concentrated hydrochloric acid 75 % and bromine water being a saturated solution of bromine in water contains nearly 97 % water, whilst concentrated sulphuric acid also always contains a certain percentage of water, 4--6. Only when concentrated sulphuric acid is used can I imagine that the small quantities of water in the preparations can be of influence, but in this case a much simpler means can be used than the thorough drying of the preparations, namely, the use of fuming sulphuric acid, so that the water with which it comes into contact is converted into sulphuric acid ( $\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{H}_2\text{SO}_4$ ). Thus fuming sulphuric acid has a stronger action than the concentrated acid.

The assertion that traces of water can interfere with the reaction, is wholly incorrect, as I shall further prove. On the contrary the best results are obtained with somewhat diluted sulphuric acid. By mixing concentrated sulphuric acid of 95 % with 10, 20, 30, 40 and 50% water, I obtained dilute sulphuric acid of 85 $\frac{1}{2}$ %, 76, 66 $\frac{1}{2}$ %,

1) F. G. KOHL, Untersuchungen über das Carotin und seine physiol. Bedeutung in der Pflanze, 1902, p. 44.

2) G. und F. TOBLER, Untersuchungen über Natur und Auftreten von Carotinen, III. Zur Bildung des Lycopins und über Beziehungen zwischen Farb- und Speicherstoffen bei *Daucus*, Ber. d. d. bot. Ges. 30. Jahrg. Heft I, 1912, p. 33.

57 and 47 $\frac{1}{2}$  % . I have experimented with sulphuric acid of varying strength in about forty cases with flowers, leaves and algae. The carotinoids, which rarely in nature occur in crystalline form, were previously separated out as crystals by means of MOLISCH'S reagent, and were successfully obtained, except in a few cases. I allowed the sulphuric acid to flow to the preparations which were in water under the cover-slip or I applied it to the preparations which lay in a minimal quantity of water on a slide. Mixing therefore always took place between the mixture used and the water in which the preparations were, and consequently there was a slight dilution of the mixture. The result of this series of experiments was that the fine blue coloration due to sulphuric acid was always shown. In most cases the reaction succeeded already with sulphuric acid of 66 $\frac{1}{2}$  or 76%, it was seldom necessary to use sulphuric acid of 85 $\frac{1}{2}$  %, and in some cases the blue colour appeared on using sulphuric acid of 57 %, e.g., in *Narcissus Pseudonarcissus* and *Cladophora*.

When stronger sulphuric acid, namely, 95 % is used, various subsidiary phenomena generally occur. Sometimes the crystals are seen to dissolve, forming blue cloudlets in the fluid, or they lose their shape and unite to form blue drops of liquid. Sometimes they dissolve and in their vicinity a precipitation of small blue drops is seen. Often the blue coloration is observed to become fainter and disappear. Commonly some of these phenomena occur together. It is difficult to say to what extent the differences in the action of sulphuric acid are caused by accidental circumstances or are connected with the chemical nature of the carotinoids, but it is certain that in the course of the reaction the latter plays an important part.

It happens, for example, in many plants, that in the same cells two kinds of crystals are separated out, which behave differently with regard to sulphuric acid. Before the action of sulphuric acid takes place, the two kinds of crystals can already be distinguished by their colour and shape, especially by the colour, which is orange-yellow or orange, and red or orange-red. The difference is, that the blue colour does not appear equally quickly in both kinds of crystals or indeed that a different degree of concentration of the sulphuric acid is required to produce it. Under the action of sulphuric acid of 66 $\frac{1}{2}$  or 76% the orange-yellow or orange crystals are immediately coloured blue and the red or orange-red ones not at all or much later. When these different crystals have about the same thickness and are in proximity in the same cells, it may be assumed that the action of the sulphuric acid takes place under the same conditions. Since the different behaviour with regard to sulphuric acid is accompanied by

differences in colour and shape and the crystals also differ in respect to other reagents and solvents, as will be further indicated, it may be assumed that the phenomenon is connected with differences of a chemical nature.

The action of concentrated sulphuric acid on dried preparations shows no trace of the different behaviour of the crystals with regard to sulphuric acid. The reaction takes place so quickly that it sometimes completely escapes observation. The treatment of dried preparations with concentrated sulphuric acid is to be deprecated, for such a method of working greatly decreases the value of the elegant reaction, which is so well suited for microscopical investigation.

The bright colour which the reaction produces is usually called blue, sometimes also blue-violet. It may be called blue, although a faint violet shade is sometimes unmistakable (compare KLINCKSIECK et VALETTE, Code des Couleurs, 426 and 451).

I have found no explanation of the reaction in the literature. HUSEMANN<sup>1)</sup> states that water causes the blue colour to disappear and unchanged carotin remains. If the blue crystals are treated with a large quantity of water, then they resume their original colour, orange-yellow or red. Sulphuric acid brings the blue colour back again.

The objects with which I have studied the sulphuric acid reaction in the manner described are the same as those with which MOLISCH's potash method was investigated (see the list in the first communication).

#### *Zinc chloride and Antimony trichloride.*

It is not only with somewhat diluted sulphuric acid, but also with saturated solutions of both zinc chloride and antimony trichloride in 25% hydrochloric acid that the crystals of the carotinoids which occur naturally in the cells or are artificially produced there, can be given a beautiful dark, persistent, blue colour. These two solutions have hitherto not been used as reagents for carotinoids. I tried them in about twenty cases. I allowed the solutions to flow to the preparations under a cover-slip. When a solution of zinc chloride was used, the preparations lay in water, but when I used a solution of antimony trichloride I first placed them in dilute hydrochloric acid in order to obviate the formation of insoluble antimony oxychloride.

The reaction did not occur equally quickly in the case of all the crystals. The orange-yellow crystals become blue before the red ones. When the zinc chloride solution was used the red crystals did not

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<sup>1)</sup> A. HUSEMANN, Ueber Carotin und Hydrocarotin, Ann. der Chem. u. Pharm. Bd. CXVII, 1861, p. 226.

always become blue. With the solution of antimony trichloride all the crystals finally became dark-blue. Generally the colour is pure blue (KL. and V. 426), but at the beginning of the reaction it is sometimes bluish-violet (476, 451). Occasionally in the use of concentrated sulphuric acid, subsidiary phenomena appear, such as the flowing together of the crystals into blue drops, solution and separation of blue droplets from the solution.

When the crystals coloured blue by means of zinc chloride or antimony trichloride are treated respectively with water or with dilute hydrochloric acid and water, the original orange-yellow or red colour reappears, although it may be somewhat less pure.

Sulphuric acid and zinc chloride solution in a more or less concentrated state strongly attack the cell-walls, but this is much less so in the case of antimony trichloride solution. This to some extent may be reckoned an advantage of the latter reagent.

There follows here a list of the organs and plants on which I have tested the two new reagents for carotinoids.

Flowers: *Trollius caucasicus* STEV., *Chelidonium majus* L., *Isatis tinctoria* L., *Spartium junceum* L., *Thermopsis lanceolata* R. BR., *Cucurbita melanosperma* A. BR., *Ferula* sp., *Asclepias curassavica* L., *Calceolaria rugosa* HOOK., *Dendrobium thyrsiflorum* RCHB. fil., *Iris Pseudacorus* L., *Narcissus Pseudonarcissus* L., *Lilium croceum* CHAIX.

Green leaves: *Chelidonium majus* L., *Urtica dioica* L.

Fruits: *Sorbus aucuparia* L., *Solanum Lycopersicum* TRN.

Root of *Daucus Carota* L.

Algae: *Cladophora* sp., *Haematococcus pluvialis* FLOT.

### *Bromine.*

The behaviour of bromine water with respect to the carotinoid crystals was studied in about twenty cases. The crystals were for the most part separated out by using MOLISCH'S reagent. Without exception a fugitive, greenish-blue colour was obtained. Generally the blue colour was clearly perceptible and only to a slight extent showed a greenish shade. In a few cases the coloration passed off quickly and the green predominated. This was so with *Chelidonium majus* and *Spartium junceum*. In the crystals of the fruit of *Solanum Lycopersicum* I saw the reddish-violet (KL. and V. 581) colour successively change into bluish-violet (476), blue, greenish-blue (386) and green, and finally this last colour faded away.

In the following cases, the crystals were investigated with bromine water.



Flowers: *Chelidonium majus* L., *Corydalis lutea* DC., *Erysimum Perofskianum* FISCH et MEY., *Isatis tinctoria* L., *Cytisus sagittalis* KOCH (*Genista sagittalis* L.), *Spartium junceum* L., *Thermopsis lanceolata* R. BR., *Cucurbita melanosperma* A. BR., *Doronicum Pardalianches* L., *Hiëracium aurantiacum* L., *Gazania splendens* HORT., *Asclepias curassavica* L., *Calceolaria rugosa* HOOK., *Dendrobium thyrsiflorum* RCHB. fil., *Iris Pseudacorus* L., *Clivia miniata* REGEL, *Lilium croceum* CHAIX, *Hemerocallis Middendorffii* TRAUTV. et MEY.

Leaf of *Urtica dioica* L.

Fruits: *Sorbus aucuparia* L., *Solanum Lycopersicum* TRN.

Root of *Daucus Carota* L.

Algae: *Cladophora* sp., *Haematococcus pluvialis* FLOT.

### *Iodine.*

With carotinoids iodine forms addition products. In about twenty cases the behaviour of iodine in potassium iodide solution was investigated with respect to the crystals of the carotinoids. By means of the potash method the latter were separated out in most cases. With iodine they became nearly always green. Often they were distinctly green, in other cases less so, and frequently they were yellowish green. In many cases the green colour appeared immediately, and sometimes not at once, but only gradually, as, namely, in the flowers of *Chelidonium majus* and *Spartium junceum*, and in the red crystals obtained in the flower of *Asclepias curassavica* and the leaf of *Urtica dioica*. Sometimes no green coloration whatever could be observed, not even after 24 hours. This was so with the flower of *Dendrobium thyrsiflorum* where, in addition to orange-yellow crystals, aggregates of orange or orange-red crystals separated out, which did not become green. The objects experimented upon with iodine in potassium iodide solution were the same as those on which bromine water was tried.

### *Solvents.*

The most suitable solvents for the microscopical investigation of the carotinoid crystals are those which can be mixed with water. The preparations can then be brought direct from water into the solvent or the solvent can be allowed to flow under a cover-slip to the preparations which are in water. Solvents which fulfil this condition are, for example, alcohol and acetone. In addition use can be made of an alcoholic soap-solution (soap-spirit of the Dutch Pharm. 4<sup>th</sup> edition, without oil of lavender) and of chloralhydrate solution

(7 in 10). With these two solutions I succeeded, in establishing for instance that in the leaves of *Urtica dioica*, the orange-yellow crystals dissolve more quickly than the red ones. The best results I obtained with phenol solutions.

According to WILLSTÄTTER and MIEG<sup>1)</sup> xanthophyll is "spielend löslich" in phenol. When liquefied phenol (10 parts by weight of phenol in loose crystals to one part by weight of water) is added under the cover-slip, the orange-yellow crystals are generally seen to dissolve very quickly, whilst the solvent becomes orange-yellow. The process of solution is often preceded by a flowing together and the formation of orange-yellow globules and masses. Other crystals, generally the red and the orange-red, the reddish-violet in the fruit of *Solanum Lycopersicum* and the orange ones which are separated out by MOLISCH's reagent in the flower of *Dendrobium thyrsoiflorum*, dissolve much more slowly. In some preparations they are dissolved after some hours, in others, kept in the solvent for several days, crystals can still be detected.

Because it is so difficult to mix with water phenol that has been liquefied by water, I have preferred for microscopic investigation a mixture of three parts by weight of phenol in loose crystals and one part by weight of glycerine. The phenomena observed are the same, but the mixing and dissolving proceed more quickly. With this solvent I have been able to show in a number of cases that the various crystals which had separated out, differed greatly in solubility. This was, for instance, the case with the flowers of *Asclepias Curassavica* and *Dendrobium thyrsoiflorum*, as also in the leaf of *Urtica dioica*.

In a few cases I experimented with a saturated aqueous phenol solution (solubility of phenol in water about 1 in 12<sup>1/2</sup>). With the orange-yellow crystals I often observed a slow deliquescence to orange-yellow globules which did not dissolve in the phenol solution.

As is stated in my first paper, the microscopical observation and separation of the crystals of carotinoids already show that there are many reasons for thinking that in the vegetable kingdom several varieties of carotinoids occur. The results obtained with various reagents and solvents, sulphuric acid, zinc chloride, antimony trichloride, bromine, iodine, and phenol solutions have further confirmed this. In my opinion the results of microscopic and micro-chemical investigations have thus been brought into agreement with macro-chemical results.

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<sup>1)</sup> RICHARD WILLSTÄTTER und WALTER MIEG, IV. Ueber die gelben Begleiter des Chlorophylls, JUSTUS LIEBIG's Annalen der Chemie, 355. Bd. 1907, p. 1.

**Botany.** -- "*On the demonstration of carotinoids in plants. Third communication: The leaf of Urtica dioica L., the flower of Dendrobium thyrsiflorum Rchb. fil. and Haematococcus pluviales Flot.*" Prof. By C. VAN WISSELINGH. (Communicated by Prof. J. W. MOLL).

(Communicated in the meeting of October 26, 1912).

In the first and second communications I have shown that carotinoids in plants present differences in the colour and shape of the crystals and in their behaviour towards reagents and solvents. It is obvious that the presence of different chemical bodies cannot be assumed when the crystals only differ in colour and shape or when only a slight difference can be observed on the addition of a reagent or a solvent. When, however, important differences in colour and shape accompany a very remarkable difference of behaviour towards reagents and solvents, then such a conclusion may be justified. I will show by means of a few striking examples that the latter case applies to the carotinoids found in plants.

#### *Leaf of Urtica dioica L.*

The substances accompanying the chlorophyll of the stinging-nettle have been accurately investigated chemically. We know from the investigations of WILLSTÄTTER and MIEG<sup>1)</sup> that two carotinoids are present in the leaves of the stinging-nettle, carotin identical with Daucus-carotin, and xanthophyll. These chemists found four times as much xanthophyll as carotin.

When leaves of *Urtica dioica* or leaf fragments are placed in MOLISCH'S reagent and examined after a few days, there is found in each cell containing-chlorophyll an aggregate of red crystals resembling small parallelograms or needles and of orange-yellow plates, which are several times more long than broad and show more or less rounded ends; sometimes a few orange-yellow curved filamentous crystals project from the aggregate. We readily observe that the orange-yellow crystals form the greater part of the aggregates. If the crystals are investigated with reagents and solvents, differences become evident. When they are treated with sulphuric acid of 76% they all finally become blue, but the orange-yellow ones are coloured first. The red ones often retain their own colour for a long time. The

<sup>1)</sup> RICHARD WILLSTÄTTER und WALTER MIEG, IV. Ueber die gelben Begleiter des Chlorophylls, JUSTUS LIEBIG'S Annalen der Chemie, 355. Bd. 1907, p. 1.

different crystals are then distinguished very clearly with sulphuric acid of 66 $\frac{1}{2}$  %, only the orange-yellow crystals become blue.

If preparations with crystals separated by the potash method are placed on the slide in a solution of chloralhydrate (7 in 10) then after a time, for example, 1 $\frac{1}{2}$  hours, the aggregates appeared much changed; the orange-yellow crystals had been dissolved and the red needles or small parallelograms remained behind, sometimes still united. After 24 hours they had not wholly disappeared from the preparations.

With soap-spirit also (Pharm. Nederl. Ed. IV, without oil of lavender) a great difference in solubility was proved. After being one day in soap-spirit the orange-yellow crystals had disappeared from the preparations, whilst the red remained behind.

I obtained a still more striking result with a solution of phenol in glycerine (3 to 1). If this mixture is allowed to flow under the cover-slip, the orange-yellow crystals are seen to dissolve quickly whilst the red ones are unchanged even after 24 hours.

The investigation of the orange-yellow and red crystals can be facilitated in the following manner. Leaf fragments are placed for two hours in a 10 % solution of oxalic acid and then put into MOLISCH'S reagent. In the tissue large red and yellow crystal-aggregates are thus formed, which can easily be studied.

On consulting the paper of WILLSTÄTTER and MIEG<sup>1)</sup> on carotin and xanthophyll, we must conclude that, of the crystals described, the red are carotin and the orange-yellow xanthophyll.

As in the leaves of *Urtica dioica* so in many other cases, in flowers, leaves and algae, I have been able to distinguish yellow, orange-yellow or orange-coloured crystals and red or orange-red ones, of different shape, which behave differently towards reagents and solvents and indeed in a more or less corresponding way. I do not doubt that in all these cases the plant contains different carotinoids side by side, in many cases probably a carotin together with a substance which belongs to the xanthophylls. I think it not improbable that the same carotin and the same xanthophyll are often found together, but I also consider that in a number of cases another carotin or xanthophyll is present. WILLSTÄTTER and ESCHER<sup>2)</sup> have already established the presence, in the fruit of *Solanum Lycopersicum*, of a carotin, lycopin, differing chemically from *Daucus*-carotin.

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<sup>1)</sup> l. c.

<sup>2)</sup> RICHARD WILLSTÄTTER und HEINR. H. ESCHER, Ueber den Farbstoff der Tomate, HOPPE-SEYLER'S Zeitschr. für Physiol. Chemie, 64. Bd. 1910, p. 47.

*The flower of Dendrobium thyrsiflorum. Rehb. fil.*

The flower of *Dendrobium thyrsiflorum* Rehb. fil., is an example of an object containing a carotinoid, differing from those so far described. After treatment by the potash method, I found in the cells orange-yellow (KLINCKSIECK et VALETTE 151) much curved filamentous crystals, orange-yellow (151) whetstone-shaped plates and large and small aggregates of brightly coloured orange (101 though inclining towards orange-red 81) thin acicular crystals. The difference in colour is very striking. Some cells are more especially filled with one shape, others with the other shape. In this case I could observe no difference on using sulphuric acid of varying strength, nor with bromine water, but on the other hand iodine in potassium iodide solution brings it out. With the latter reagent the orange-yellow crystals at once become a fine green. The orange-yellow aggregates suffer no change of colour whatsoever, not even after 24 hours. The contrast in the colour of the crystals is very striking. So far as concerns their solubility in a solution of phenol in glycerine (3 to 1) the crystals also differ much. When the solvent is allowed to flow under the cover-slip, the orange-yellow crystals are at once seen to deliquesce, and form with the solvent yellow globules which dissolve entirely. On the other hand the orange-coloured aggregates do not at first show any signs of dissolving. Sometimes they are seen in the midst of the globules that are formed. Finally all the orange aggregates can be seen in the yellow solution of the orange-yellow crystals. Slowly the orange crystals dissolve also. If the preparations are placed for one day in the mixture of phenol and glycerine, the orange crystals also dissolve.

Because of the difference in colour, different behaviour towards iodine in potassium iodide solution and different solubility in phenol, I conclude that two different carotinoids occur in the flower of *Dendrobium thyrsiflorum*. The one of these which is to some extent reddish-orange in colour, is a carotinoid that is not common in plants. Such a carotinoid I have found only in *Dendrobium thyrsiflorum*. Its colour and other properties makes me inclined to think that it belongs to the xanthophylls rather than to the carotins.

*Haematococcus pluviialis Flot.*

The colouring matter of this interesting alga has been investigated by ZOPF<sup>1)</sup>. The result of his enquiry was that it possesses not one but two

<sup>1)</sup> W. ZOPF, COHN's Hämatochrom ein Sammelbegriff, Biologisches Centralblatt, XV. Bd. 1895, p. 417.

colouring matters, which must be considered to be carotinoids. ZOPF found a yellow carotinoid such as is commonly found in green plants and a red one to which the alga is indebted for its frequently dark blood- or brown-red colour and for its name. ZOPF succeeded in separating the two colouring matters in the following way. The crude alcoholic extract of the alga was saponified with caustic soda. The chlorophyll was thus changed into a sodium compound, the fat into a soap and glycerine, the yellow carotinoid was set free and the red one converted into a sodium compound insoluble in water. When the saponification products after dilution with water, were treated with petroleum ether, the yellow carotinoid was removed, whilst the sodium compound of the red one separated out. After purifying the sodium compound the carotinoid was set free by means of dilute sulphuric acid, it was taken up in ether and investigated spectroscopically. The red carotinoid differs spectroscopically from the yellow, in colour and in the colour of its solutions, and also in its power of combining with alkalis and alkaline earths.

*Haematococcus pluvialis* has recently also been investigated by JACOBSEN<sup>1)</sup>. By means of MOLISCH'S potash method he obtained separation of crystals, but on the other hand he was unsuccessful with dilute acids and with TSWETT'S resorcinol solution. The accuracy of ZOPF'S results remained undecided.

Mr. JACOBSEN was kind enough to send me a culture of *Haematococcus pluvialis* on agar, and thus I was given an opportunity of studying this remarkable alga and of confirming the above mentioned conclusions of JACOBSEN. As is clearly shown by his beautiful plates, the aplanospores differ very much as regards colour; some have a green content, in consequence of the chlorophyll they contain, others are green at the periphery and red in the centre, whilst in others again the green of the chlorophyll is entirely masked and there seems to be only a red content. The red colouring matter is combined with a liquid fatty substance or, more accurately, is dissolved in it. This substance occurs in the form of globules in the cell-content.

As is to be expected, aplanospores which at first sight show differences, yield different results on investigation. In the green spores orange-yellow crystals were quickly separated out by MOLISCH'S reagent; generally these are shaped like curved needles, which are often united into bundles; sometimes orange-yellow crystal plates were also observed. In addition to these plates, there were also a

<sup>1)</sup> H. C. JACOBSON. Die Kulturbedingungen von *Haematococcus pluvialis*, *Folia Microbiologica*, I, 1912, p. 24 et seq.

few small red plates, shaped like parallelograms. On the addition of sulphuric acid of 66½ or 76 % the orange-yellow crystals become blue without any deliquescence to globules or solution being observed. This takes place when sulphuric acid of 95 % is used. The small red crystals, shaped like parallelograms are not so quickly coloured blue as the orange-yellow ones or a more concentrated acid must be applied in order to colour them blue. The crystals also behave differently with respect to phenol glycerine. The orange-yellow quickly dissolve in it whilst the red remain undissolved. The orange-yellow crystals behave therefore like xanthophyll-crystals and the red ones like carotin-crystals. The investigation of the green aplanospores therefore gives no special result. Two carotinoids are found to accompany chlorophyll, an orange-yellow one and in small quantity a red one, as is usual in green plants.

In those aplanospores which are more or less red in colour there are found after treatment with MOLISCH'S reagent reddish-violet crystal aggregates and, frequently, curved band shaped crystals. I now leave out of further consideration the small red crystals shaped like parallelograms. The crystals do not seem to be so easily separated out in the red aplanospores as in the green ones. It is advisable to allow MOLISCH'S reagent to act for at least some days in order to decompose the fatty substance which tenaciously retains the colouring matter. If any of the fat remains behind, the investigation becomes more difficult in consequence.

By means of sulphuric acid of 66½, the reddish-violet crystals become blue, also with 76% sulphuric acid, but in this case the action is accompanied by partial solution, which sometimes is preceded by deliquescence. The surrounding medium becomes blue. The behaviour of the reddish-violet crystals towards sulphuric acid of varying strength is therefore different from that of the orange-yellow crystals. In a solution of phenol in glycerine (3 to 1) the reddish-violet crystals easily dissolve, and colour the solvent dark reddish-violet.

The crystals were not at one time of an orange-yellow colour, and at another time reddish-violet, but in many cases they oscillated between the two colours. Orange-yellow and reddish-violet crystals were never observed side by side in the same cell. These facts and the solution in 76 % sulphuric acid, as described, led me to suppose that the reddish-violet crystals were perhaps mixed crystals composed of two carotinoids. I then tried to separate them with solvents, and succeeded. The crystals often completely dissolve in acetone or absolute alcohol; the orange-yellow carotinoid remains in solution, but the other quickly separates out again in the cells in the form

of numerous small violet platelets. The experiment can be made in a test tube and also on a microscope slide. Under the microscope the process of solution, the yellow-coloration in and round the cells and the separation of the violet platelets can be seen.

The phenomena observed can be explained in the following way. The orange-yellow carotinoid is fairly easily soluble in acetone or absolute alcohol; the other one is practically insoluble, but its solubility is increased by the presence of the orange-yellow one, with which it forms mixed crystals. A solution of both is produced in the cells, and is quickly diluted, and this brings about that the carotinoid insoluble in acetone or in absolute alcohol separates out. I am confirmed in this opinion by an observation of ZOPF<sup>1</sup>). When he extracted the yellow carotinoid from the aqueous solution of the saponification products with petroleum-ether, the other separated out beneath the petroleum-ether.

I cannot distinguish any definite form in the violet platelets. They behave in the following way towards reagents and solvents. With sulphuric acid of 66½% the colour is not modified or only slightly so, but with 76% sulphuric acid the crystals quickly take a blue colour and this is speedily followed by dissolution. In a saturated zinc chloride solution in 25% hydrochloric acid and in a saturated antimony trichloride solution in 25% hydrochloric acid they become blue, then the crystals generally deliquesce to blue globules and dissolve. The solutions are bluish-violet or blue. With bromine water a very transitory bluish-green colour is observed. In a solution of phenol in glycerine (3 to 1) the crystals dissolve, whilst the solvent becomes bright reddish-violet.

If the reddish-violet crystals obtained from the red aplanospores by means of MOLISCH'S reagent are compared with those separated out from alcohol and acetone and with the orange-yellow ones obtained from the green aplanospores by MOLISCH'S reagent, then the first mentioned crystals, so far as their properties are concerned, must be placed between the other two, and this strengthens my belief that they are mixed crystals.

I must here remark that according to ZOPF<sup>2</sup>) the violet-red or blood-red carotinoid enter into combination with potassium hydroxide. On this account it should be assumed that the reddish-violet crystals, separated out with MOLISCH'S reagent contain the potassium compound of the carotinoid and that the crystals obtained with acetone and alcohol consist of this compound. In the microchemical investigation

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<sup>1</sup>) l. c. p. 419.

<sup>2</sup>) l. c. p. 419.



I have obtained no indication which points to this. When I treated the crystal platelets got from acetone or alcohol, with dilute sulphuric acid for 24 hours at the ordinary temperature I found them unchanged and moreover their solubility in various solvents remained the same. However this may be, ZOPF's results and mine obtained by different methods agree in this that in *Haematococcus pluvialis* more than one carotinoid occurs. According to ZOPF there are two, whilst I have succeeded in crystallising out three in the cells and in separating each from the other two.

Finally I must add a few experimental details. By cultivating *Haematococcus pluvialis* in various solutions, I obtained cultures with different aplanospores, both green and red. I cultivated the alga in the two following solutions:  $\text{KNO}_3$  0.01,  $(\text{NH}_4)_2\text{HPO}_4$  0.01,  $\text{MgCl}_2$  0.01,  $\text{Na}_2\text{SO}_4$  (hydrated) 0.01,  $\text{H}_2\text{O}$  100 and  $\text{NH}_4\text{NO}_3$  0.02,  $\text{K}_2\text{HPO}_4$  0.02,  $\text{MgSO}_4$  0.02,  $\text{H}_2\text{O}$  100<sup>1</sup>). In the former solution most of the aplanospores had a green content, in the latter a red one, and this was an advantage in the investigation. I used a centrifuge for transferring *Haematococcus* from one solution to another and for washing out the material, which sank to the bottom on centrifuging so that the solution to be replaced could be poured off.

It results from this paper and the two previous ones, that my conclusions differ completely from those of TAMMES and of KOHL. The assumption, that only one carotinoid occurs in the vegetable kingdom, is not based on sufficient evidence. It was the result of microscopic and micro-chemical research. Nevertheless I believe that such investigation may contribute to our knowledge of carotinoids, provided that it be carefully carried out. I have found, for instance, that when different carotinoids occur in a plant or organ, it is in many cases at least possible, to distinguish them, that unknown ones can be detected (*Dendrobium thyrsiflorum*) and that sometimes a greater number can be demonstrated than has hitherto been possible by other means (*Haematococcus pluvialis*). The results I have obtained are in agreement with the macro-chemical investigation (*Urtica dioica*). When the quantity of material is insufficient for the application of other methods, a microscopical and micro-chemical inquiry is still practicable and moreover demands comparatively little time. The botanist who concerns himself with such work, should however consider, that it is impossible to solve by means of a few colour-reactions difficult chemical problems, such as, for example, the

<sup>1</sup>) H. C. JACOBSEN, l. c. p. 8.

identification of the carotinoids of different plants. As ZOPF<sup>1)</sup> justly says careful macro-chemical investigation alone can lead to decisive results in such cases.

**Chemistry.** — “*Equilibria in ternary systems I*”. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of October 26, 1912).

On the equilibria occurring in ternary systems between liquid and vapour different theoretical<sup>2)</sup> and experimental<sup>3)</sup> investigations have already appeared previously. We will now discuss a few cases where, in addition to liquid and vapour, solid substances occur also.

*The system F L G.*

We choose for *F* a ternary compound and will assume that the three components occur in the vapour.

We now choose at a definite constant temperature *T* such a pressure *P* that no vapour can form. The isotherm can then consist only of the saturation line of the solid substance *F*. This saturation line is a closed curve surrounding the point *F* like the closed curve of Fig. 1, for instance.

On reduction of *P* a gas region appears somewhere and at the same time a heterogeneous region separating the gas region from the liquid region. In Fig. 1 the gas region is indicated by *G*, the liquid-region by *L*; the drawn line is the liquid-line, the dotted one the gas- or vapour line of the heterogeneous region. The straight lines drawn in this heterogeneous region unite the liquids with the vapours with which they can be in equilibrium.

We now have in Fig. 1 two homogeneous regions, namely the liquid region *L* and the gas region *G*; in addition we find two heterogeneous regions.

In one of them a mixture dissociates into  $L + G$ ; we will call

1) W. ZOPF, Zur Kenntnis der Färbungsursachen niederer Organismen (Dritte Mitteilung), Beiträge zur Physiol. u. Morph. niederer Organismen, 1892, Erstes Heft, p. 36.

2) J. D. VAN DER WAALS. These Proc. Vol. IV p. 448, 539, 681; Vol. V p. 1, 121, 225. (1902).

F. A. H. SCHREINEMAKERS. Zeitschr. f. phys. Chem. 36 257, 413, 710 (1901) 37 129 (1901) 38 227 (1901) 43 671 (1903)

B. M. VAN DALFSEN. Dissertation, Amsterdam. (1906).

3) F. A. H. SCHREINEMAKERS. Zeitschr. f. Phys. Chem. 39 485, 40. 440, 41. 331 (1902), 47 445, 48 257 (1904).

B. M. VAN DALFSEN. l.c.

this the heterogeneous region LG. In the other takes place a dissociation into solid F and a liquid saturated with F of the saturation line of F; we will call this the heterogeneous region FL.

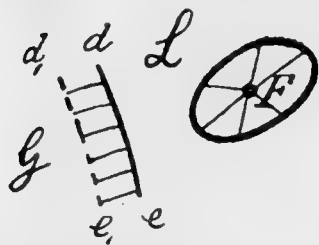


Fig. 1.

If we imagine the liquid- and vapour surface of the  $\zeta$ -surface to be introduced above Fig. 1, it is obvious that the solid substance F can be also in equilibrium with a whole series of ternary vapours, which equilibria, however, are in the present case all metastable yet. It is also obvious that these vapours must form in Fig. 1 a closed curve surrounding point F, which curve, however, has been omitted from the figure. We will call this curve "vapour saturation curve" of the solid substance F. This curve surrounds the heterogeneous region FG which, however, is still quite metastable.

Hence in Fig. 1 we distinguish :

the saturation line of F.

the vapour saturation line of F (metastable).

the vapour- and liquid-line of the heterogeneous region LG.

the vapour region (G) and the liquid-region (L.)

and the heterogeneous regions LG, LF and GF, the latter of which is metastable.

The vapour region G can form within as well as without the saturation line of F; on further reduction of the pressure there may occur also several vapour regions first isolated from each other and afterwards amalgamating. Moreover, in the system liquid + gas there may occur either binary or ternary vapour pressure maxima or minima or stationary points so that different cases are to be distinguished. We will first take the case that there occurs neither a binary or ternary maximum or minimum nor a stationary point so that the gas region appears in one of the apexes of the component-triangle and the liquid region disappears in one of the other apexes.

In Fig. 1 the gas region is, therefore, formed outside the saturation line of F; on reduction of the pressure, the different curves of Fig. 1 will change in form and position. As a rule, a small change in pressure only causes an exceedingly small change in the solubility of a solid substance; hence, the saturation line of F will alter but little on change of pressure within very wide limits. This, however, as we will notice presently, becomes different when we get near to the melting point of F so that the saturation line of F is only still a small curve.

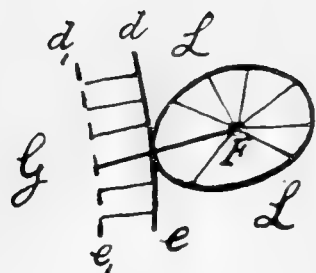


Fig. 2.

The influence of a change in pressure on a liquid and vapour region is, however, great in comparison with that on the saturation line of F. When the pressure decreases, the gas region extends and the liquid region contracts; the heterogeneous region LG shifts, therefore, in Fig. 1 towards the heterogeneous region FL. Hence, on reduction of pressure, there will occur a pressure as represented in Fig. 2 where the liquidline and the saturation line of F will meet in a point M so that the equilibrium  $F + L_M + G_{M_1}$  appears. The three points F, M, and  $M_1$  as follows readily from the indicatrix theorem, are situated on a straight line. With the aid of the two sheets of the  $\zeta$ -surface it is also easy to see that the non-drawn vapour saturation line of F in Fig. 2, must meet the vapour line in  $M_1$ .

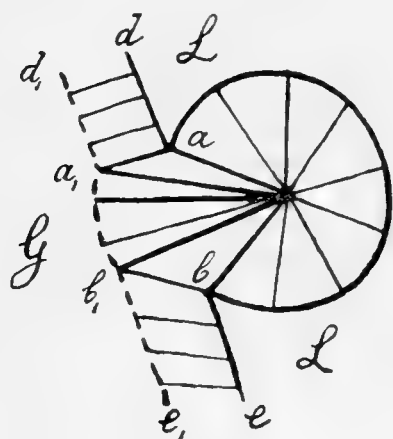


Fig. 3.

On further decrease of the pressure, the saturation line of F and the liquidline intersect each other in two points; these intersecting points are represented in Fig. 3 by a and b; in the solid substance the letter F is omitted.

From a contemplation of the liquid sheet and vapour sheet of the  $\zeta$ -surface it follows at once that with each intersecting point of the saturation line of F and the liquidline is conjugated an intersecting point of the vapour saturation line of F and the vapour line. As the saturation line of F and the liquidline intersect each other in the points a and b, the vapour saturation line of F and the vapour line must intersect each other in the two points  $a_1$  and  $b_1$ . The curve  $a_1 b_1$  is the vapour saturation line of F, the vapour line consists of the two parts  $e_1 b_1$  and  $a_1 d_1$  which are, of course, connected with a metastable branch not drawn in the figure.

At the pressure contemplated here, two three-phase equilibria  $F + L + G$  therefore occur, namely:



On further reduction of the pressure, the heterogeneous region LG shifts more and more in such a direction that the vapour region becomes larger and the liquid-region smaller. At a certain pressure, the liquidline will pass through the point F, after which this gets situated within the heterogeneous region. We then obtain an isotherm as in Fig. 4 which does not differ essentially from that of Fig. 3.

On further decrease of the pressure, the points  $a$  and  $b$  and consequently  $a_1$  and  $b_1$  will at a definite pressure coincide; here we first assume that  $F$  then still lies within the heterogeneous region  $LG$ . We then obtain an isotherm like in Fig. 5 in which we must

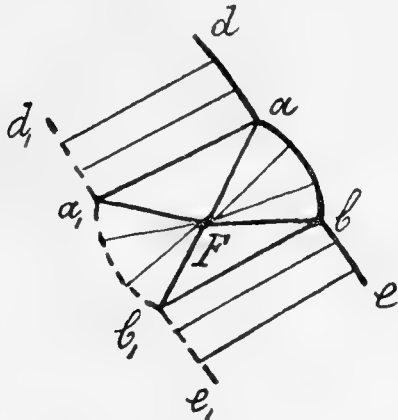


Fig. 4.

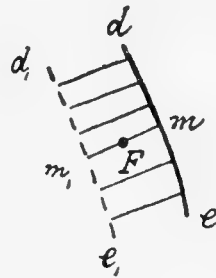


Fig. 5.

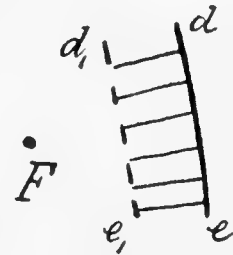


Fig. 6.

imagine  $m$  to be formed by the coincidence of  $a$  and  $b$ , and  $m_1$  by the coincidence of  $a_1$  and  $b_1$ . It is obvious that  $m_1$ ,  $F$  and  $m$  must lie on a straight line and that the non-drawn and metastable saturation line of  $F$  must meet the curve  $d e$  in  $m$  and that the vapour saturation line of  $F$  must meet the curve  $d_1 e_1$  in  $m_1$ .

On further decrease of pressure the saturation and vapour saturation curves of  $F$  arrive quite within the heterogeneous region  $LG$ ;  $F$  cannot, therefore, occur any longer in the solid condition but splits into vapour + liquid; the composition of the vapour is now represented by a point of the vapour line  $d_1 e_1$ , that of the liquid by a point of the liquidline  $d e$ . Both points lie with  $F$  on a straight line.

On reducing the pressure still further we obtain, when the gas region has extended itself over the point  $F$ , isotherms like those in Fig. 6. The vapour saturation line of  $F$  has now disappeared, the saturation line of  $F$  can, however, still exist but then represents only metastable solutions and has, therefore, been omitted from the figure.

From the foregoing views, it now follows at once that the liquid as well as the vapour of the system  $F + L + G$  trace a closed curve, like in Fig. 7 and that on each of these lines occurs a point of maximum and of minimum pressure. As the points of the curves of Fig. 7 all appertain to a same temperature but to different pressures, we may call Fig. 7 an isothermic — polybaric diagram.

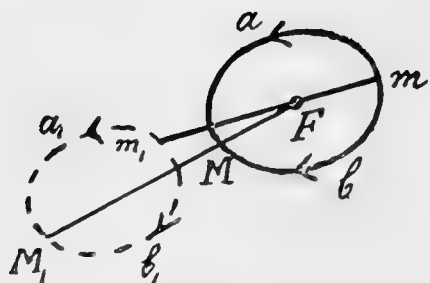


Fig. 7.

The curve  $M a m b$  represents the solutions which, at a given temperature are saturated with  $F$  under their own pressure; the compositions of the vapours are indicated by the curve  $M_1 a_1 m_1 b_1$ . We may, therefore, call the curve  $M a m b$ , the isothermic saturation line of  $F$  under its own vapour pressure and  $M_1 a_1 m_1 b_1$  its con-

jugated vapour line; where no mistake is possible we will omit the adjunct "isothermic".

As a rule, the saturation line of  $F$  at a certain constant pressure  $P$  and the saturation line of  $F$  under its own vapour pressure will differ but little, so that, practically, we may substitute the one for the other; as to exceptions for temperatures in the vicinity of the melting point of the compound  $F$  to them we will refer later.

We have already stated above that the saturation line of  $F$ , under its own vapour pressure, must exhibit a point with a vapour pressure maximum and another with a vapour pressure minimum; the first is represented in Fig. 7 by  $M$ , the second by  $m$ . On the conjugated vapour line, there occur, of course also two points  $M_1$  and  $m_1$  of which  $M_1$  represents the vapour with the vapour pressure maximum and  $m_1$  that with the vapour pressure minimum. The arrows on both curves indicate the direction of the increasing vapour pressure.

The points  $F$ ,  $M$  and  $M_1$  are, of course, situated on a straight line and agree with the isothermic-isobaric diagram of Fig. 2; the points  $F$ ,  $m$  and  $m_1$  which are of course also situated on a straight line, agree with the isothermic-isobaric diagram of Fig. 5.

We have assumed above that on lowering the pressure the diagrams 3, 4 and 5 succeed each other, or in other words that the points  $a$  and  $b$  of Figs. 3 and 4 had already coincided in a point  $m$  of Fig. 5 before the vapour region had extended to over  $F$ . If, however, the vapour line has already passed point  $F$  before  $a$  and  $b$  of Fig. 3 or 4 coincide we get an isotherm as in Fig. 8 which, however, does not differ essentially from Fig. 3 or 4. On further reduction of the pressure Fig. 8 is converted into Fig. 9. The vapour saturation line of  $F$  now meets the vapour line  $e_1 d_1$  in  $m_1$ ; the saturation line of  $F$  not drawn in Fig. 9 meets the liquidline  $ed$  in  $m$ . The vapour saturation line of  $F$  represents the stable, the saturation line of  $F$  the metastable conditions. The points  $F$ ,  $m$  and  $m_1$  are, of course, again situated as in Fig. 5 on a straight line; as, however, these points are situated, in the two figures, differently in regard to each.

other, the reaction between solid  $F$ , liquid  $m$  and gas  $m_1$  is in these two cases also different.

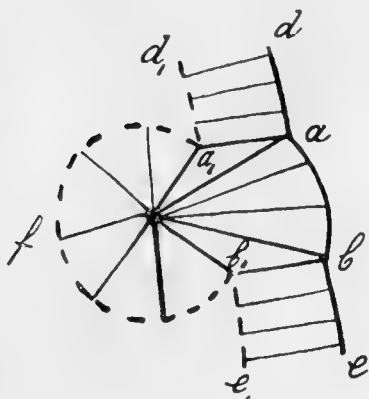


Fig. 8.

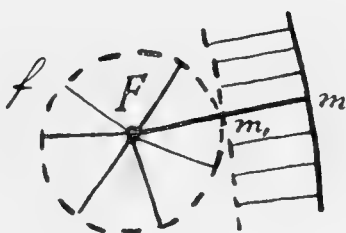


Fig. 9.

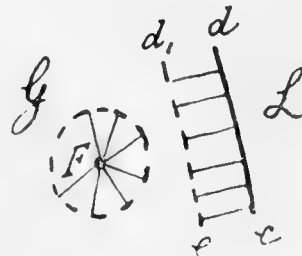


Fig. 10.

On reducing the pressure still further, the two regions  $L G$  and  $F G$  separate and diagrams as in Fig. 10 are obtained. The non-drawn saturation line of  $F$  represents metastable conditions only; solutions saturated with  $F$  can, therefore, occur only in the metastable condition at this pressure.

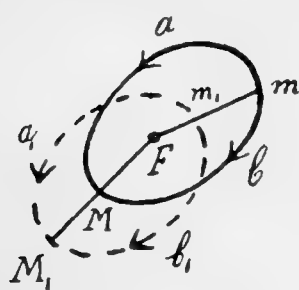


Fig. 11.

The case is, however, different with the vapours saturated with  $F$ ; these all occur in the stable condition and are represented by the closed vapour saturation line of Fig. 10.

By a further fall in pressure this vapour saturation line of  $F$  becomes continuously smaller; at the vapour pressure of the compound  $F$  it contracts to a point, namely point  $F$ , and on further reduction in pressure it disappears.

Hence, the liquid as well as the vapour of the system  $F + L + G$  again trace a closed curve (Fig. 11).  $M a m b$  is the saturation line of  $F$  under its own pressure,  $M_1 a_1 m_1 b_1$  its conjugated vapour line. On the one curve the pressure in  $M$  is maximum and in  $m$  minimum, on the other curve in  $M_1$  and  $m_1$ ; the pressure thus increases in both in the direction of the arrows.

The two Figs. 7 and 11 exhibit a great resemblance to each other; yet they differ in different respects such as for instance, in the situation of the points  $F$ ,  $m$  and  $m_1$  in regard to each other. This causes that in Fig. 7 the point  $F$  is situated outside and in Fig. 11 within the vapour line.

When deducing the previous diagrams we have assumed that on change of pressure, the liquidline of the heterogeneous region moves more rapidly than the saturation line of  $F$  or what amounts to the same that the vapour line of the heterogeneous region  $L G$  moves quicker than the vapour saturation line of  $F$ .

Although this is the case generally, it no longer holds good if we take a temperature close to the melting point of F. The saturation line of F then surrounds a comparatively small region which on change of pressure, can rapidly extend, or possibly contract. The saturation line of F will then move more rapidly than the liquid-line of the region L G. We will now distinguish two cases in one of which the substance expands on melting whilst in the other case it contracts.

*F expands on melting.* An increase in pressure (at constant T) will cause a solidification of the molten F, a decrease in pressure a fusion of solid F. On decrease in pressure, the isothermic saturation line of F will consequently contract rapidly and disappear in the point F. We now start from Fig. 1 and assume that, on lowering the pressure, the saturation line of F contracts at first rather slowly and then more rapidly; its movement is more rapid than that of the liquid line of the heterogeneous region L G.

If now the movement of the saturation line of F is slower than that of the liquid line, Fig 1 may be converted into Fig. 2 and then into Fig. 3 from which are then formed either the Figs. 4, 5 and 6 or the Figs. 8, 9 and 10. If however, after the isotherms have assumed a form as in Fig. 3, the movement of the saturation line becomes more rapid than that of the liquidline, then, after the appearance of the isotherms of Fig. 3, those of Fig. 2 and 1 reappear. On reduction of the pressure we then get a series of isotherms such as:

fig: 1  $\rightarrow$  fig. 2  $\rightarrow$  fig. 3  $\rightarrow$  fig. 2a  $\rightarrow$  fig. 1a

in which the figures occurring after fig. 3 are indicated by 2a and 1a. Fig. 2 and 2a resemble each other with this great difference, however, that in fig. 2a the saturation line of F is much smaller and that the liquid and vapour lines of the heterogeneous region lie more adjacent to F than in fig. 2. The same applies to fig. 1a in regard to fig. 1. Between fig. 2 and 2a there is also still this difference that Fig. 2 applies to the maximum and Fig. 2a to the minimum pressure of the system F + L + G. We will therefore assume that in fig. 2a the letters M<sub>1</sub> and M of fig. 2 have been replaced by m<sub>1</sub> and m.

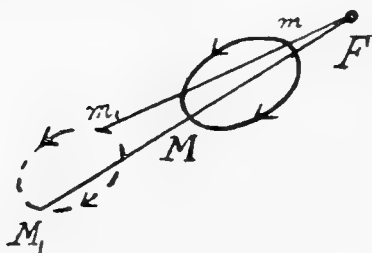


Fig. 12.

From the previous considerations it now follows at once that the saturation line of F under its own vapour pressure must be situated as in fig. 12; contrary to this same curve in fig. 7 and 11 it does not surround the point F which represents the solid phase with which its solutions are saturated. We will, therefore



call the saturation line of F in figs. 7 and 11 a circumphased and that of fig. 12 an expahsed one.

*F contracts on melting.* An increase in pressure (at constant T) will, therefore cause a fusion of solid F, a decrease of pressure a solidification of molten F. On decrease of pressure the isothermic saturation line of F will consequently form first of all in F and then extend at first rapidly and then slowly.

We now start from such a pressure that a heterogeneous region L.G does exist, but not yet the saturation line of F. We then have fig. 1 from which we must, however, leave out the saturation line of F. On lowering the pressure, the liquid line shifts towards F and we assume that it has already just passed the point F when the saturation line of F appears in the point F. The isotherm then has a form as in fig. 5 or 6 in which, however, we must assume the curve d e to be very close to F. On further reduction of pressure the saturation line of F now rapidly extends round the point F and overtakes the liquid-line so that at a definite pressure they come into contact with each other. We then obtain an isotherm as in fig. 5 or 9. In fig. 5 however, we must imagine the saturation and the vapour saturation lines of F to be drawn and in such a manner that the first curve comes into contact with e d in m, the second curve with  $d_1 e_1$  in  $m_1$ . In Fig. 9 we must also imagine the saturation line of F coming into contact with the curve d e in m.

On further reducing the pressure fig. 4 or 8 are formed and as the velocity of the saturation line of F now becomes smaller than that of the liquid-line, these are again converted into fig. 5 or 9. Hence on reduction of pressure we obtain a succession of isotherms such as :

fig. 5  $\rightarrow$  fig. 4  $\rightarrow$  fig. 5a or fig. 9  $\rightarrow$  fig. 8  $\rightarrow$  fig. 9a.

in which fig. 5a differs from fig. 5, and fig. 9a from fig. 9 in this way, that in the figures indicated by a the liquid line e d is removed further from point F. Also, as the fig. 5 and 9 occur at higher pressures than the fig. 5a and 9a the letters m and  $m_1$  must be considered as being replaced by M and  $M_1$ .

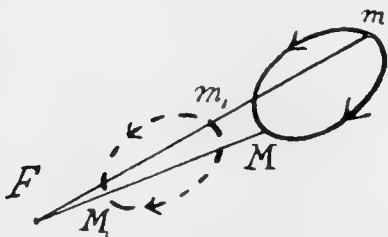


Fig. 13.

From these considerations it now follows that the saturation line of F must exist under its own pressure as in fig. 13, hence expahsed; the correlated vapour line may be expahsed as well as circumphased and may also be situated on the other side of F.

The case may also occur that the satu-

ration line under its own pressure and its correlated vapour line get each reduced to a point. Both these points then lie with F on a straight line.

This case will occur when the saturation line of F and the liquid line when meeting each other in a point (fig. 2 in M, in fig. 5 and 9 in m) move at that moment from that point towards and from F with the same velocity. The same then applies to the vapour line and vapour saturation line of F which also meet in a point ( $M_1$  in fig. 2 and  $m_1$  in fig. 5 and 9). This equality of velocity has, of course, also a physical significance, which we will look for.

We represent the composition and the volume of the solid substance F by  $\alpha$ ,  $\beta$  and  $v$ , that of the liquid by  $x$ ,  $y$  and  $V$  and that of the gas by  $x_1$ ,  $y_1$ ,  $V_1$ .

The equation of the saturation line of F is then given by:

$$[(\alpha - x)r + (\beta - y)s] dx + [(\alpha - x)s + (\beta - y)t] dy = -\Delta V \cdot dP \quad (1)$$

and that of the liquid line of the heterogeneous region LG by:

$$[(x - x_1)r + (y - y_1)s] dx + [(x - x_1)s + (y - y_1)t] dy = V_{0.1} dP \quad (2)$$

in this:

$$\Delta V = V - v + (\alpha - x) \frac{\partial V}{\partial x} + (\beta - y) \frac{\partial V}{\partial y}$$

$$V_{0.1} = V - V_1 + (x_1 - x) \frac{\partial V}{\partial x} + (y_1 - y) \frac{\partial V}{\partial y}$$

As the two curves (1) and (2) come into contact with each other  $x$  and  $y$  in (1) and (2) are the same and then we have:

$$\frac{\beta - y}{\alpha - x} = \frac{y_1 - y}{x_1 - x} = \frac{\beta - y_1}{\alpha - x_1} = \mu.$$

If now we write (1) and (2) in the form:

$$(r + \mu s) dx + (s + \mu t) dy = -\frac{\Delta V}{\alpha - x} dP$$

$$(r + \mu s) dx + (s + \mu t) dy = \frac{V_{0.1}}{x - x_1} dP$$

we notice that the above mentioned circumstance will appear as:

$$-\frac{\Delta V}{\alpha - x} = \frac{V_{0.1}}{x - x_1}.$$

After substitution of the values  $\Delta V$  and  $V_{0.1}$  we can write for this also:

$$(\alpha - x_1) V + (x - \alpha) V_1 + (x_1 - x) v = 0$$

or

$$(\beta - y_1) V + (y - \beta) V_1 + (y_1 - y) v = 0.$$

This means that the change in volume which can occur in the reaction between the three phases  $F$ ,  $L$ , and  $G$ , which are in equi-

librium with each other is *nil*. The reaction between the three phases therefore takes place without a change in volume. We will return to this later.

We may summarise the above as follows:

The isothermic-isobaric saturation and vapour saturation curves of a solid substance F are, at all temperatures and pressures, circumphased and disappear (are formed) in the point F.

The saturation curves of a solid substance F under their own vapour pressure are at a lower temperature circumphased; at a definite temperature, one of them passes through the point F after which, at higher temperatures, they become exp phased, then they disappear in a point, if in the reaction between the three phases no change of volume occurs. This also applies to the vapour lines appertaining to the saturation lines under their own pressure which can, however, be already exp phased at lower temperatures.

In fig. 14 are drawn some saturation lines under their own vapour pressure with their appertaining vapour lines for different tempera-

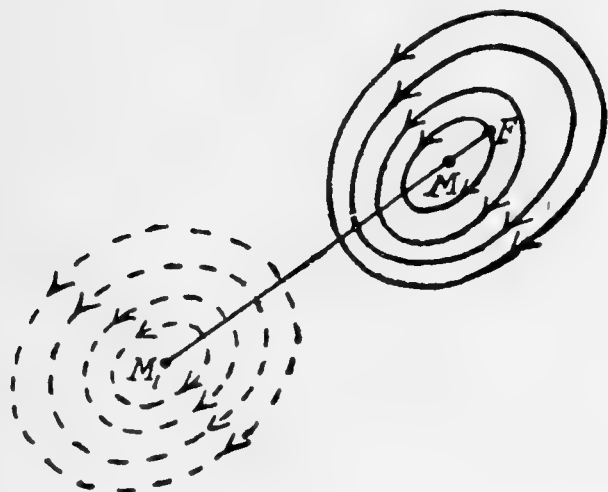


Fig. 14.

On each of these curves occurs a point with a maximum and one with a minimum vapour pressure which, however, are not indicated in the Fig. although the arrows indicate the directions in which the pressure increases. These points are situated of course, in such a manner, that the line which unites two points with a maximum or minimum pressure of curves of the same temperature, passes through the point F. The saturation line under its own vapour pressure disappears in the point M; the appertaining vapour-line in the point M, both points lie with F on a straight line.

In fig. 14 the curves of different temperatures are all united in a plane; if, however, we imagine a temperature axis drawn perpendicular to this plane and also the curves in space according to their temperatures, two surfaces are formed, namely the saturation surface, under its own pressure of F and the appertaining vapour surface. The first has its top in M, the second in M<sub>1</sub>; the line MM<sub>1</sub> is situated horizontally. It is evident that the point F does not coincide with the top M of the saturation surface under its own vapour pressure but is situated somewhat lower and that the points M<sub>1</sub>, M and F lie in a same vertical plane. (To be continued).

**Botany.** — “*Dichotomy and lateral branching in the Pteropsida*”.

By Mr. J. C. SCHOUTE. (Preliminary communication). <sup>1)</sup>

(Communicated in the meeting of Oct. 26, 1912).

In 1900 and more recently <sup>2)</sup> JEFFREY argued that the correspondence in structure of Filicales, Gymnosperms and Angiosperms justified the union of these three groups into a higher group, that of the Pteropsida.

Palaeontological research has later rendered this conclusion more probable <sup>3)</sup>.

When on this account we assume a closer relationship between these groups, there naturally still remain many great differences between them; one of these is in the method of branching. For whilst the Gymnosperms and Angiosperms without exception branch by means of axillary buds (apart from adventitious buds), we find the ferns are typically dichotomous <sup>4)</sup>. METTENIUS <sup>5)</sup> described long ago in ferns lateral buds in every kind of position (axillary, next to the insertion of the leaf, under the insertion, half on the stem and half on the petiole) but all this has been explained by VELENOVSKÝ as due to the formation of “stable adventitious buds <sup>6)</sup>”. The distinction between dichotomy and lateral branching has always been considered by all writers to be of great phylogenetic importance.

An investigation on branched tree-ferns has led me to the idea that there may perhaps be no difference in principle between these various modes of branching; in other words, that dichotomous branching would be, in its essence, the same as the lateral branching of ferns or Angiosperms. The fine material, mostly collected by Mr. KOORDERS, on which this investigation has been made, will be described exactly in the detailed publication. Here I only remark that in these trees ordinary dichotomy can sometimes take place, as a reaction to certain pathological processes, with a normal

<sup>1)</sup> A detailed paper, illustrated by plates, will appear on this subject in the *Recueil des Travaux botaniques néerlandais*.

<sup>2)</sup> E. C. JEFFREY. *The Morphology of the Central Cylinder in the Angiosperms*; *Canadian Inst. Trans.*, Vol. 6, 1900. — *The Structure and Development of the Stem in the Pteridophyta and Gymnosperms*; *Philos. Trans. R. Soc. London*, Vol. 195, 1902.

<sup>3)</sup> See e. g. D. H. SCOTT, *Studies in fossil. Botany*, 2nd Ed. London 1908/09, p. 638.

<sup>4)</sup> J. VELENOVSKÝ. *Vergleichende Morphologie der Pflanzen*. Prag 1905, p. 245.

<sup>5)</sup> G. METTENIUS. *Ueber Seitenknospen bei Farnen*, *Abhandl. math-phys. Classe k. Sächs. Ges. d. Wiss.* Bd. 5, 1861, p. 611.

<sup>6)</sup> *l.c.* p. 247.

angular leaf, such as, according VĚLENOVSKÝ, characterizes dichotomy in ferns <sup>1)</sup>).

In this process however, one of the two branches may also be smaller than the other, in which case the larger branch places itself entirely in the prolongation of the base. These cases gradually pass into such in which one branch forms in every respect a prolongation of the base, and the other is placed next to an ordinary leaf of the stem as a thin branch or small lateral bud; this leaf we may then still regard as the angular leaf of the dichotomy.

From these observations we may deduce that probably all branchings in ferns, including those by means of VĚLENOVSKÝ's "stable adventitious buds", are to be referred to one and the same process and also that it is not permissible to consider the lateral buds of ferns as adventitious buds. It then further becomes highly probable that the axillary branching of Gymnosperms and Angiosperms is due to the same process. The only points of difference between the lateral branching of ferns and that of these groups, are that in ferns the bud is not always placed above the insertion of the leaf and that by no means all leaves produce buds.

In the Conifers we find already an intermediate stage to the extent that by no means all leaves have axillary buds, whilst in the cycads another intermediate stage seems to be found, for in this group the rare non-adventitious buds appear to be placed, not above, but next to the corresponding leaf <sup>2)</sup>).

If this is so then, the normal dichotomy, which occurs in rare cases among Angiosperms <sup>3)</sup> is a different, new process, a dichotomy of the second order, as it were.

<sup>1)</sup> l. c. p. 246.

<sup>2)</sup> E. WARMING, *Undersøgelser og Betragtninger over Cycadeerne*. Oversigt K. Danske Vidensk. Selsk. Forh. 1877 p. 91. — H. Graf von SOLMS LAUBACH, *Die Spoorfolge der Stangeria und der übrigen Cycadeen*. Bot Zeitung 48, 1890, p. 197.

<sup>3)</sup> See my article "Ueber die Verästelung bei monokotylen Bäumen II. Die Verästelung von *Hyphaene*", in *Recueil des Trav. botan. Néerl.* Vol. 6 1909 p. 211. The opinion expressed there on p. 232 that the dichotomy of *Hyphaene* is the first case described in the literature of dichotomy in a phanerogam is incorrect since CHURCH in his "Relation of phyllotaxis to mechanical laws" (London 1904) in the "notes and errata" at the end of the book (p. 352) already described the dichotomy of fasciated heads of *Helianthus*.

**Mathematics.** — “*On loci, congruences and focal systems deduced from a twisted cubic and a twisted biquadratic curve*”. II.  
Communicated by Prof. H. K. DE VRIES.

(Communicated in the meeting of Oct. 26, 1912).

11. We found in § 1<sup>1)</sup> a surface  $\Omega^6$  as locus of the points  $P$  for which the chord  $a$  of  $k^3$  and the two chords  $b$  of  $k^4$  are coplanar; in the plane of those three chords then lies a ray  $s$  of the tetrahedral complex discussed in the preceding §<sup>2)</sup>, so that the rays  $s$  corresponding to the points  $P$  of  $\Omega^6$  form a congruence contained in the complex; we wish to know this congruence better.

Through an arbitrary point  $P$  of space pass six rays of the congruence, thus  $\mu = 6$ ; for all rays  $s$  through that point form a quadratic cone, the complex cone (§ 10), and the foci corresponding to the edges of this cone lie on the ray  $s$  of  $P$ ; this intersects  $\Omega^6$  in 6 points and the rays  $s$  conjugated to these pass through  $P$ . The number  $\mu$  is called the order of the congruence.

Exceptions we find only for the points of  $k^4$  and in the 4 cone vertices. If  $P$  lies on  $k^4$  then the conjugated line  $s$  is the tangent in  $P$ , which now belongs itself to the complex cone of  $P$ , for it is generated as line of intersection of the two polar planes of  $P$  itself with respect to  $\Phi_1, \Phi_2$ , which planes coincide with the tangential planes to the two quadratic surfaces. The tangent  $s$  to  $k^4$  is now however at the same time tangent to  $\Omega^6$  and it contains therefore besides the point of contact only 4 points of  $\Omega^6$ ; thus besides the tangent only 4 rays of the congruence pass through  $P$ , from which ensues that the tangent itself counts double.

The four cone vertices bear themselves quite differently. To  $T_1$  e.g. are conjugated as rays  $s$  all the lines of the plane  $T_2 T_3 T_4 = \tau_1$ , which plane intersects  $\Omega^6$  in a curve  $k^6$  of order 6 containing  $T_2, T_3, T_4$  as single points, the points of intersection with  $k^3$  on the other hand as nodal points; to each point of the curve a ray  $s$  through  $T_1$  is conjugated, so that through  $T_1$  pass an infinite number of rays of the congruence forming a cone. This cone can be determined more closely as follows. As of an arbitrary line  $s_1$  in  $\tau_1$  the two conjugated lines pass through  $T_1$ , the ray  $s_1$  corresponding to the points of that ray  $s_1$  form a quadratic cone; now  $s_1$  intersects the curve  $k^6$  in 6 points, thus the quadratic cone must intersect the cone to be found in 6 edges.

Let us consider the point of intersection of  $s_1$  with the edge  $T_3 T_4$

1) See *Proceedings* of Oct. 26th, 1912, p. 495.

2) l. c. p. 509.

of the tetrahedron. The two polar planes of this point now pass not only through  $T_1$ , but also through  $T_2$ , because the point itself lies now not only in  $\tau_1$  but also in  $\tau_2 = T_1T_3T_4$ ; so the quadratic cone contains the edge  $T_1T_2$  and of course for the same reason  $T_1T_3$  and  $T_1T_4$ . These same edges lie also on the cone to be found and that as fourfold ones, which is easy to see when we consider e.g. the line  $T_3T_4$ . This line intersects  $k^6$  in  $T_3, T_4$  and in four points more; to  $T_3$  all lines of  $\tau_2$  are conjugated and thus also particularly all lines of  $\tau_2$  through  $T_1$ , so that this plane (and for the same reason the two other tetrahedral planes through  $T_1$ ) separate themselves from the cone; however, for each of the 4 remaining points of intersection the conjugated ray  $s$  is determined and identical with  $T_1T_2$ , so that this line is indeed for the cone under discussion a fourfold edge. So the quadratic cone and the cone under discussion have in common:

1. the three fourfold edges of the latter, 2. the 6 rays  $s$ , conjugated to the points of intersection of  $s_1$  with  $k^6$ , thus altogether  $3 \times 4 + 6 = 18$  edges; so the cone under discussion is of order nine. If finally we see that this cone possesses three double edges too, formed by the rays  $s$  conjugated to the three nodal points of  $k^6$  lying in  $k^3$ , we can comprise our results as follows:

*For the congruence of the rays  $s$  corresponding to the points of  $\Omega^6$  the four cone vertices are singular points, as through these points pass instead of 6, as in the general case,  $\infty^1$  rays of the congruence; these form at each of those 4 points in the first place three pencils situated in the three tetrahedral planes through that point, and in the second place a cone of order nine with three double edges and three fourfold edges, the latter coinciding with the three tetrahedral edges through that point.*

The cone of order nine must intersect the tetrahedral plane  $\tau_4 = T_1T_2T_3$  in nine edges, four of which lie united in  $T_1T_2$ , four others in  $T_1T_3$ , so that only one is left; the latter is to be regarded as the line  $s$  more closely conjugated to point  $T_4$ , and it will change its position if  $k^6$  changes its form, and passes through  $T_4$  in an other direction.

The complete nodal curve of the surface of tangents of  $k^4$  consists of four plane curves of order four lying in the four tetrahedral planes and every time with 3 vertices of that tetrahedron as nodes; let us now regard in particular the nodal curve lying in  $\tau_1$ . Through a point  $P$  of this pass two tangents of  $k^4$  representing the two chords  $b$  through that point; the line connecting the two contact points passes through  $T_1$  and is an edge of the doubly

projecting cone having this point as vertex, and from this all follows easily that that edge of the cone is the line  $s$  conjugated to the point  $P$  of the nodal curve. The nodal curve now intersects  $k^6$  in 24 points, of which 6 however coincide two by two with  $T_2, T_3, T_4$ ; the lines  $s$  conjugated to the 18 remaining ones are the lines of intersection of the cone of order nine with the doubly projecting cone at the vertex  $T_1$ .

The surface of tangents of  $k^4$  is of order eight, it contains the 4 just mentioned plane curves of order 4 as nodal curves and the four cone vertices as fourfold points; it intersects  $\Omega^6$  in a curve of order 48 having the cone vertices as fourfold points, the 24 points of intersection with  $k^3$  and the 4 times 18 points of intersection on the 4 nodal curves as nodal points. For an arbitrary point of this curve a chord  $a$  of  $k^3$  and 2 chords  $b$  of  $k^4$  are complanar; one of these two chords  $b$  however is a tangent of  $k^4$ . For one of the 24 nodal points on  $k^3$  the same holds, as is easy to see; for each of the  $4 \times 18$  remaining nodal points on the other hand a chord  $a$  of  $k^3$  is complanar to 2 tangents of  $k^4$ .

12. We now determine the second characteristic number, the class  $\nu$  of the congruence formed by the rays  $s$  conjugated to the points of  $\Omega^6$ , i. e. the number of rays of the congruence in an arbitrary plane. The locus of all foci of all the rays  $s$  lying in an arbitrary plane  $\alpha$  is according to § 10 a twisted cubic through the four cone vertices; this intersects  $\Omega^6$  in 18 points, but to these belong the four cone vertices. To each of the 14 remaining ones one ray  $s$  is conjugated, lying in the assumed plane; to a cone vertex on the other hand all rays of the opposite tetrahedral face are conjugated, and therefore also the line of intersection of that face with  $\alpha$ , so that if we like we can say that in each plane lie 18 congruence rays, among which, however, then always appear the lines of intersection with the four tetrahedral planes. So we prefer to say that *in an arbitrary plane lie 14 congruence rays and that from the complete congruence the 4 fields of rays situated in the four tetrahedral planes separate themselves.*

In § 8 we found that the double tangential planes of the surface  $\Omega_{18}$  discussed in § 7 of class 18 envelop a developable  $\Delta_9$  of class 9; they are nothing else than the focal planes of the points of  $k^3$ . The lines  $s$  they contain belong to the congruence we are discussing, and these rays count double in the congruence because  $k^3$  is for  $\Omega^6$  a nodal curve; let us find the locus of these double rays.

If a point  $P$  describes the curve  $k^3$ , then each of its two polar planes



$\pi_1, \pi_2$  with respect to  $\Phi_1, \Phi_2$  envelops the reciprocal figure of a cubic curve, i. e. a developable of class 3, and the tangential planes of these two developables are conjugated through the points  $P$  one by one to each other; for, a tangential plane  $\pi_1$  of the first developable has only one pole  $P$  and this again only one polar plane with respect to  $\Phi_1$ . Now the lines  $s$  are the lines of intersection of the conjugated tangential planes of the two developables; they form a scroll the order of which appears to be 6. Let us namely assume a line  $l$ ; through a point  $P$  of this line pass 3 tangential planes  $\pi_1$  of the first developable, and to these three planes  $\pi_2$  are conjugated; if these intersect the line  $l$  in three points  $Q$ , then to one point  $P$  three points  $Q$  are conjugated, but of course inversely too; through each of the 6 coincidences passes one line  $s$ , so the line  $l$  intersects the demanded surface in 6 points.

For each of the three points of intersection of  $k^3$  with one of the four tetrahedral faces the corresponding line  $s$  passes through the opposite vertex; the four cone vertices are therefore threefold points of the surface. Moreover the surface possesses a nodal curve cut by each generatrix in  $6 - 2 = 4$  points and which proves to be of order 10; the four cone vertices are as points of intersection of 3 generatrices of the surface also threefold points of the nodal curve.

The order of the nodal curve we determine again as in § 9 with the aid of SCHUBERT'S formula:

$$2 \cdot \varepsilon\beta = \varepsilon\sigma + 2 \cdot \varepsilon g,$$

by conjugating each generatrix of the scroll as ray  $g$  to all others as rays  $h$ . The symbol  $\varepsilon g$ , the number of coinciding pairs where  $g$  intersects an arbitrary line, is 6, viz. equal to the order of the surface; the question is now how great is  $\varepsilon\sigma$ , the number of pairs  $gh$  of which the components lie at infinitesimal distance and intersect each other; these are evidently the torsal lines of the surface. We shall show that their number is 8.

The rays  $s$  conjugated to the points of a line  $l$  describe a regulus through the four cone vertices (§ 4) and so they cross each other all, then too when they lie at infinitesimal distance; they can intersect each other only when line  $l$  is itself a ray  $s$  (§ 10); however, they then intersect each other all and that in the same point, viz. the focus of  $s$ . If thus two rays  $s$  corresponding to two points of  $k^3$  are to intersect each other, then their connecting line must be a ray  $s$ ; and if moreover these rays are to lie at infinitesimal distance then the line connecting the points must be a tangent of  $k^3$ ; so the question is simply this how many tangents of  $k^3$  are rays of the

tetrahedral complex. Now according to one of the theorems of HALPHEN a complex of order  $p$  and a scroll of order  $n$  have  $pn$  generatrices in common; the tetrahedral complex is quadratic, the surface of tangents of  $k^3$  is of order 4 and so the number of common rays is 8; so  $\varepsilon\sigma = 8$ . From this ensues  $2 \cdot \varepsilon\beta = 8 + 2 \times 6 = 20$ ,  $\varepsilon\beta = 10$ . Now  $\varepsilon\beta$  represents the class of a plane section of our scroll of order 6; by applying the first PLÜCKER formula for plane curves (§ 9) we thus find  $\sigma = 10$ , a number we can control with the aid of

$$\sigma p + \varepsilon g + \varepsilon\beta = gh \quad (\S 9); \text{ viz.}$$

$$\sigma p + 6 + 10 = 36$$

$$\sigma p = 20,$$

and this is twice the order of the nodal curve as we proved in § 9. Summing up we thus find: *The nodal rays of our congruence form a scroll of order 6 with 8 torsal lines and therefore also 8 pinch points lying on a nodal curve of order 10 which is intersected by each generatrix in 4 points and having the vertices of the four doubly projecting cones of  $k^4$  as threefold points.*

§ 13. We shall inquire in this § into the scroll of the rays  $s$  of our congruence, resting on an arbitrary line  $l$  and in particular on a ray  $s$ . All rays  $s$  intersecting  $l$  form a congruence (2,2); for the quadratic complex cone with an arbitrary point of space as vertex intersects  $l$  in 2 points, so that through that point 2 rays of the congruence pass; and an arbitrary plane contains of the complex cone of the point of intersection with  $l$  likewise 2 rays, so that in an arbitrary plane lie likewise 2 rays of the congruence. An exception is made by the points *on*  $l$ , which are vertices of quadratic cones of rays of the congruence and the planes *through*  $l$  containing an infinite number of rays of the congruence, which evidently envelop a conic because two of them pass through any point of the plane. Among these planes are four, which are distinguished from the others, because the conic which they bear breaks up into a pair of points, and dualistically related to these are 4 points on  $l$  whose quadratic cone breaks up into a pair of planes; the *planes* are those through  $l$  and the 4 cone vertices, the *points* are the points of intersection of  $l$  with the four tetrahedral planes. In the plane  $lT_1$  e.g. according to § 10 all the rays through  $T_1$  belong to the complex, so the conic in this plane must degenerate into  $T_1$  and one other point; or expressed in other words: of the two rays of the congruence through a point of this plane one passes through the fixed point  $T_1$ , so the second must also pass through a fixed point.

This point is a certain point of the line of intersection of the plane  $lT_1$  with the face  $\tau_1$  lying opposite  $T_1$ ; for, for an arbitrary point  $P$  of  $\tau_1$  the complex cone breaks up into the pencil with vertex  $P$  lying in  $\tau_1$  and a pencil with vertex  $P$  lying in a certain plane through  $P$  and  $T_1$ , and inversely for a plane through  $T_1$ , so e.g. our plane  $lT_1$ , the complex conic breaks up into point  $T_1$  and a second point lying on the line of intersection of that plane with  $\tau_1$  (§ 10). So the four singular points on  $l$  are therefore nothing else but the points of intersection with the four tetrahedral planes.

Two congruences according to the theorem of HALPHEN possess in general only a finite number of common rays; however, the congruence discussed above and the one deduced out of the points of  $\Omega^6$  possess an infinite number, therefore a scroll; for *all* complex rays  $s$  cutting  $l$  belong to the former, and every time 6 of these through a point of  $l$  belong according to § 4 to the second; the two congruences have thus a scroll in common for which the line  $l$  is a sixfold line. As furthermore according to § 12 there lie in each plane 14 rays of the second which as rays  $s$  cutting  $l$  also belong to the former (*and therefore, as we now discover, envelop a conic*) the scroll to be found is a  $\Omega^{20}$  of order twenty and with a nodal curve which by each plane through the sixfold line  $l$  is cut in  $\frac{1}{2} \cdot 14 \cdot 13 = 91$  points not lying on  $l$ .

If a point  $P$  describes a line  $l$ , then the corresponding line  $s$  describes a regulus through the 4 cone vertices (§ 4); and if we wish to construct for that same point  $P$  the complex cone, then according to § 10 we must determine the lines  $s$  which correspond to the points of the line  $s$  conjugated to  $P$ ; *from this ensues that the regulus formed by the lines corresponding to the points  $P$  of  $l$  is the locus of the points  $P$  whose conjugated rays form the congruence of the rays  $s$  which intersect  $l$ . And so furthermore from this ensues that the curve  $k^{12}$  of order twelve along which that regulus and  $\Omega^6$  intersect each other, is the locus of the points  $P$  whose conjugated lines  $s$  form the just found surface  $\Omega^{20}$ .*

Each generatrix  $s$  of the regulus contains 6 points of  $\Omega^6$  or therefore of  $k^{12}$ ; the corresponding lines  $s$  are the six generatrices of  $\Omega^{20}$  issuing from the focus conjugated to the generatrix  $P$  of the regulus on the sixfold line  $l$ . The curve  $k^{12}$  admits 6 nodal points, viz. the points of intersection of the regulus with  $k^3$ ; the line  $s$  of the regulus through such a point intersects  $\Omega^6$  in two coinciding points, from which ensues that through the point  $P$  on  $l$  conjugated to that line  $s$  really only 5 rays  $s$  pass instead of 6; one of these, however, viz. the one corresponding to the nodal point of  $k^{12}$ , is a generatrix

of the surface of the double rays of the congruence (§ 12), and thus evidently a double generatrix of  $\Omega^6$ . So: *the 6 points of intersection of  $l$  with the surface of the double rays of the congruence deduced from  $\Omega^6$  are double generatrices of  $\Omega^{20}$ .*

The curve  $k^{12}$  passes through the 4 cone vertices and the lines  $s$  corresponding to them fill the tetrahedral faces lying opposite; so we can ask how  $\Omega^{20}$  bears itself with respect to those faces. We now have separated in § 12 of the complete congruence deduced from  $\Omega^6$  the four fields of rays in the tetrahedral faces; if we thus follow  $k^{12}$  through the vertex  $T_1$ , then to all points on either side of  $T_1$  every time a completely determined ray intersecting  $l$  is conjugated; by this also in  $\tau_1$  one ray is determined, so that  $\Omega^{20}$  has simply one of its generatrices in  $\tau_1$  and therefore this plane as an ordinary tangential plane. The cone vertices on the contrary are themselves singular points of  $\Omega^{20}$ . Our curve  $k^{12}$  namely cuts  $\tau_2$  in 12 points lying on a conic and at the same time on the section  $k^6$  of  $\Omega^6$  with  $\tau_1$ , to which belong the three cone vertices  $T_2, T_3, T_4$ ; the rays  $s$  corresponding to these lie, it is true, according to the above, respectively in  $\tau_2, \tau_3, \tau_4$ , but they do not pass through  $T_1$  (if let us say  $s$  conjugated to  $T_2$  had to pass e.g. through  $T_1$  it would have to pass for the same reason through  $T_3$  and  $T_4$ ), however the rays corresponding to the remaining 9 points of intersection do; so in the plane  $T_1l$  nine generatrices of  $\Omega^{20}$  pass through  $T_1$ ; *they are the lines of intersection of this plane with the cone of order nine, on which lie according to § 11 the rays  $s$  which are conjugated to the points of intersection of  $\Omega^6$  with  $\tau_1$ .* The same holds of course for the planes through the remaining vertices and  $l$ .

In such a plane the conic which must be touched by the 14 generatrices of  $\Omega^{20}$  degenerates, as we have seen at the beginning of this §, into a pair of points; *so in each of these four planes not only nine generatrices pass through a cone vertex, but also the five remaining ones pass through another fixed point, lying in the opposite face. The vertices are thus for the nodal curve of  $\Omega^{20} \frac{1}{2} \cdot 9 \cdot 8 = 36$ -fold points, the other points  $\frac{1}{2} \cdot 5 \cdot 4 = 10$ -fold points.* If we add these  $36 + 10$  points to the 45 points generated by the intersection of the two groups of 5 and respectively 9 generatrices lying in a plane through a cone vertex and  $l$ , we find back the 91 points of the beginning of this §.

If we add to the figure, as we are now studying it, another arbitrary line  $m$ , then to this also belongs a regulus through the 4 cone vertices cutting the regulus conjugated to  $l$  in a curve of order four through the vertices; this biquadratic curve has with  $\Omega^6$  twenty-four points in common among which again the cone vertices; if we set these

apart for reasons more than once mentioned, then there remain twenty; the rays  $s$  corresponding to these rest on  $l$  as well as on  $m$ , i. e. the rays resting on  $l$  form a surface  $\Omega^{20}$ . This in order to control the result.

§ 14. We shall now try to determine the order of the nodal curve of  $\Omega^{20}$ , which is according to the preceding equal to 91, augmented by the number of points unknown for the present, with which that curve rests on  $l$ ; this number is connected with other numbers which we must also calculate to be able to find the former, and to this a deeper study is necessary of  $\Omega^{20}$ , as well as of the figures which are in relation with this surface.

A scroll possesses in general a certain number of pinch points and torsal lines, and those of  $\Omega^{20}$  can be divided into two kinds which bear themselves very differently in the following considerations. To the first kind we reckon the torsal lines whose pinchpoint lies on  $l$  but whose torsal plane does not pass through  $l$ ; to the second kind the dualistically opposite, thus those whose pinchpoint does not lie on  $l$  (thus on the nodal curve to be investigated), but whose torsal plane for it does pass through  $l$ .

A third kind might be a combination of the two others, torsal-lines, whose pinchpoint lies on  $l$  and whose torsal plane passes through  $l$ ; we shall however show that these do not appear on  $\Omega^{20}$ .

We can get some insight in the appearance of these torsal lines if we return to the regulus and the curve  $k^{12}$  of the preceding §;  $k^{12}$  contains the foci of all generatrices  $s$  of  $\Omega^{20}$ , and the regulus is the locus of all the rays  $s$ , which are conjugated to the points  $P$  of  $l$ . Moreover lie in a plane through  $l$  fourteen generatrices of  $\Omega^{20}$  and the foci of these lie on a cubic curve through the four cone vertices. Let us now consider the generatrices of the regulus and the curve  $k^{12}$ . A generatrix  $s_r$  of the regulus intersects  $\Omega^6$  in six points and these lie on  $k^{12}$ , for  $k^{12}$  is the intersection of  $\Omega^6$  with the regulus; the rays  $s$  corresponding to these six points are the generatrices of  $\Omega^6$ , which pass through a same point  $P$  of  $l$ , viz. the focus of  $s_r$ . If however  $s_r$  has two coinciding points in common with  $k^{12}$ , then two of the six generatrices through  $P$  coincide, and this can happen in two ways. The curve  $k^{12}$  has namely 6 nodal points (viz. on  $k^3$ ), and through each of these passes a line  $s_r$  which has with  $k^{12}$  besides the nodal point only four points in common; of the six generatrices of  $\Omega^{20}$  through the focus  $P$  of  $s_r$  two coincide and that in a double generatrix of  $\Omega^{20}$ , the number of which, as we know, (§ 13) amounts to 6. Those double lines can be regarded as “full

coincidences" in the sense of SCHUBERT, i. e. as coinciding lines whose point of intersection as well as whose connecting plane is indefinite; so they satisfy the definition we have given above of torsal lines of the first kind.

In the second place now however an  $s_r$  can touch the curve  $k^{12}$ ; in this case the two coinciding rays  $s$  conjugated to the point of contact form a "single coincidence", i. e. two coinciding rays whose point of intersection and whose connecting plane both remain definite; the point of intersection lies on  $l$ , the connecting plane however does not pass in general through  $l$ , for then it would be necessary that in the point where  $s_r$  touches the curve  $k^{12}$  at the same time also one of the cubic curves through the vertices were to touch that curve, which can of course in general not be the case; so we find torsal lines of the first kind. However, if there really were torsal lines of the third kind, then there would have to be among the points of contact of the rays  $s_r$  with  $k^{12}$  also some where at the same time a cubic curve were to touch  $k^{12}$ ; these particular points of contact would then give rise to the torsal lines of the third kind.

The cubic conjugated to a plane  $\lambda$  through  $l$  may have with  $k^{12}$  two coinciding points in common; in this case two generatrices lying in the same plane  $\lambda$  coincide. This happens in the first place for those planes  $\lambda$  whose conjugated cubic passes through one of the six nodal points of  $k^{12}$ , and so we find again the nodal lines of  $\Omega^{20}$ ; this, however, also takes place if a cubic touches  $k^{12}$ , and then we find a torsal line of the second kind; for the two rays  $s$  conjugated to the point of contact coincide whilst their connecting plane  $\lambda$  remains definite. Their point of intersection lies in general not on  $l$ , because the point of contact of  $k^{12}$  with the cubic is in general not a point of contact of  $k^{12}$  with a generatrix  $s_r$  of the regulus; for those points however where that might be the case we would find torsal lines of the third kind.

We calculate the complete number of points, where a line of the regulus has two coinciding points in common with  $k^{12}$ , with the aid of the formula of SCHUBERT:

$$\varepsilon = p + q - g^1)$$

which relates to a set of  $\infty^1$  pairs of points. We can now indeed obtain such a set by conjugating on each line of the regulus each of the six points  $k^{12}$ , regarded as a point  $p$ , to the five others, which are then named  $q$ ; each line of this kind bears then thirty pairs, because each of the six points of  $k^{12}$  lying on it can be conjugated succes-

<sup>1)</sup> SCHUBERT l. c. p. 44.

sively as point  $p$  to the five others (which are then called  $q$ ), and the whole number is  $\infty^1$ . The quantity  $p$  in the formula points to the number of pairs, where the point  $p$  lies in a given plane; now this plane intersects  $k^{12}$  in twelve points, which we can all regard as points  $p$ ; through each of these passes one line of the regulus containing still five other points of  $k^{12}$ , which we shall call  $q$ ; it is then clear that there are 60 pairs  $pq$  whose component  $p$  lies in a given plane. The symbol  $q$  has the same meaning as  $p$ , in this case for the points  $q$ ; however, as in our case each point of  $k^{12}$  can be a  $p$  as well as a  $q$ , the quantity  $q$  is also  $= 60$ . Finally the letter  $g$  indicates the number of pairs whose connecting line intersects a given line; now that given line intersects only two lines of the regulus, on each of which 30 pairs  $pq$  are situated;  $g$  is therefore 60, and in this way we find for  $\varepsilon$ , the number of coincidences,

$$\varepsilon = 60 + 60 - 60 = 60.$$

So there are sixty lines of the regulus containing two coinciding points of  $k^{12}$ ; 6 of them correspond to the double generatrices of  $\Omega^{20}$ , but a closer investigation shows us that these must be counted double; the remaining forty-eight are tangents of  $k^{12}$  and correspond to torsal lines: *so  $\Omega^{20}$  contains forty-eight torsal lines of the first kind.*

The formula  $\varepsilon = p + q - g$ , or written as:  $p + q = g + \varepsilon$ , is namely deduced by assuming a system of  $\infty^1$  pairs of points  $p, q$  and by projecting these out of a line  $l$ . If a plane  $\lambda$  through  $l$  contains  $p$  points  $p$ , we can connect the points  $q$  conjugated to these by planes with  $l$ , so that  $p$  planes are conjugated to  $\lambda$ ; if inversely a plane  $\lambda$  contains  $q$  points  $q$ , then to this plane  $q$  others are conjugated, and thus is generated a correspondence  $(p, q)$  with  $p + q$  coincidences, which are evidently furnished by means of the coincidences of the pairs of points themselves ( $\varepsilon$ ) and by the pairs of points whose connecting line intersects  $l$ .

Let us now apply this to our case. A plane  $\lambda$  intersects  $k^{12}$  in twelve points  $p$ ; to each of these the five points  $q$  are conjugated lying with  $p$  on a generatrix of the regulus, so that to  $\lambda$  sixty other planes are conjugated. A plane  $\lambda$  through a nodal point  $D$  of  $k^3$  however contains of  $k^{12}$  besides  $D$  only ten more points, which give rise to fifty planes; so the ten remaining ones must be furnished by  $D$  itself. Now the generatrix of the regulus through  $D$  intersects  $\Omega^6$  besides in  $D$  only in four points more, the planes through these and  $l$  count double in the correspondence, because  $D$  itself counts double in the plane  $lD$ , but this furnishes only four planes counting double, or eight single ones; so the two missing ones must coincide with the plane  $lD$ , i. e.  $lD$  is a double plane counting double (and

likewise a fourfold "branchplane") Q. E. D. In § 17 we shall see a confirmation of the considerations given here.

§ 15. In order to be able to point out the eventual existence of the torsal lines of the third kind, we must include a new auxiliary surface in our consideration, which we deduce from the tetrahedral complex. All complex rays lying in one and the same plane envelop a conic which also touches the four tetrahedral planes, and indeed in § 13 we have already drawn attention to the fact that the fourteen generatrices of  $\Omega^{2^0}$  lying in a plane  $\lambda$  through  $l$  are the tangents of a conic; the auxiliary surface which we must introduce to find the torsal lines of the third kind is the locus of these conics, thus the locus of the complex conics lying in the planes  $\lambda$  through  $l$ . In each plane  $\lambda$  lies one and through each point of  $\lambda$  pass two of these conics, as is easy to prove. For, let us imagine an arbitrary plane  $\lambda$  and an arbitrary point  $P$  on  $l$ , then  $\lambda$  intersects the complex cone of  $P$  in two rays  $s$ , and these are the tangents out of  $P$  to  $k^2$  lying in  $\lambda$ ; therefore if  $k^2$  is to pass through  $P$  then the two tangents out of  $P$  must coincide, and this takes place in the two tangential planes through  $l$  to the complex cone. *The locus to be found is therefore an  $\Omega^4$  with double line  $l$ .*

If a surface possesses a double line it is an ordinary phenomenon that only a part is efficient, the rest parasitical; so applied to our case that through certain points of  $l$  two real conics go, through others two conjugated imaginary ones, and through the limiting points between both groups two coinciding ones; for the surface we have here under discussion those limiting points are the points of intersection of  $l$  with the four tetrahedral planes. Let us namely assume the point of intersection  $s_1$  of  $l$  with  $\tau_1$ . The complex cone of  $S_1$  breaks up into two planes, viz.  $\tau_1$  and a plane through  $S_1$  and  $T_1$  cutting  $\tau_1$  along a line  $s_1$  through  $S_1$ ;  $s_1$  is nothing else but the generatrix which  $\Omega^{2^0}$  has in common with  $\tau_1$ . Now the tangential planes through  $l$  to this degenerated cone coincide in the plane  $ls_1$ , which bears a complex conic touching  $\tau_1$  in  $S_1$  (with tangent  $s_1$ ); this conic is the only one passing through  $S_1$ .

Of great importance for our surface  $\Omega^4$  are furthermore the planes through  $l$  and the four cone vertices. We know i.a. that of the fourteen generatrices of  $\Omega^{2^0}$  in the plane  $lT_1$  nine pass through  $T_1$  and the other five through a point  $T_1^*$  lying in  $\tau_1$ , and really the complex conic in this plane breaks up into the pair of points  $T_1$ ,  $T_1^*$ , which means for the surface  $\Omega^4$  that it is intersected by the plane  $lT_1$  (except in the nodal line  $l$  of course) in the line



$T_1 T_1^*$ , counted double, whilst the tangents to this conic degenerated into a double line, thus the complex rays in this plane can only go through  $T_1$  and  $T_1^*$ ; the four planes  $l T_i$  ( $i = 1, \dots, 4$ ) touch  $\Omega^4$  along the four lines  $T_i T_i^*$  ( $i = 1, \dots, 4$ ), and the 8 points  $T_i, T_i^*$  ( $i = 1, \dots, 4$ ), are nodal points of  $\Omega^4$ .

The nodal point  $T_1^*$  lies in  $\tau_1$  and is characterized by the property that its complex cone breaks up into the plane  $\tau_1$  and the plane  $T_1^* l$ , so that each ray through  $T_1^*$  cutting  $l$  is a complex ray. Let us assume e.g. the plane  $T_1^*, T_2^*, T_3^*$ ; this cuts  $l$  in a certain point  $L$  and according to the preceding the lines  $LT_1^*, LT_2^*, LT_3^*$  are complex rays. But if three complex rays lying in one plane pass through the same point, then the complex curve in that plane must degenerate into a pair of points, and this takes place only for the planes through the four cone vertices; so the plane  $T_1^* T_2^* T_3^*$  passes through a vertex, in our notation  $T_4$ . And with this we have proved the following property: *the eight nodal points of  $\Omega^4$  can be divided into two groups of four,  $T_1, \dots, T_4$  and  $T_1^*, \dots, T_4^*$ , and the four tetrahedra having these points as vertices are simultaneously described in and around each other.*

The surface  $\Omega^4$  is one of those already found and described by PLÜCKER in his "Neue Geometrie des Raumes", Part 1, § 6, p. 193 etc., on the occasion of his general investigations of quadratic complexes.

We shall now intersect the surfaces  $\Omega^4$  and  $\Omega^{20}$  with each other. The section which must be of order 80 consists in the first place of the line  $l$  to be counted twelve times, because  $l$  is for  $\Omega^4$  a double line and for  $\Omega^{20}$  a sixfold line; the residual section is thus a curve of order  $80 - 12 = 68$ . Now there lie in a plane  $\lambda$  through  $l$  fourteen generatrices of  $\Omega^{20}$ , and these touch a conic lying on  $\Omega^4$ ; so the residual section is a curve having with a plane  $\lambda$  through  $l$  fourteen points in common. However, we must keep in view that the two surfaces touch each other in every ordinary point which they have in common outside  $l$ ; so the residual section must be a curve to be counted twice, from which ensues that its order must be 34; as it has outside  $l$  with a plane  $\lambda$  only fourteen points in common, it must have with  $l$  itself 20 points in common. It then goes 9 times through each of the four points  $T_i$  ( $i = 1, \dots, 4$ ), and 5 times through each of the four points  $T_i^*$  ( $i = 1, \dots, 4$ ) because these points are respectively 9- and 5- fold points of  $\Omega^{20}$  (§ 13) and nodal points of  $\Omega^4$ ; the curve counted double has then 18- and resp. 10-fold points, as should.

How does now a point of intersection of the curve found just

now with  $l$  make its appearance? An arbitrary point is generated when in the plane  $\lambda$  through that point and  $l$  a generatrix of  $\Omega^{20}$  and a conic of  $\Omega^4$  touch each other; so a point on  $l$  is generated when in a certain plane  $\lambda$  through  $l$  a generatrix of  $\Omega^{20}$  and a conic of  $\Omega^4$  touch each other exactly on  $l$ ; then through the point of contact, however, pass two coinciding tangents of the conic, thus two coinciding complex rays; or, in a better wording, whilst in an arbitrary plane  $\lambda$  through each of the 14 points of  $l$  lying at the same time on generatrices of  $\Omega^{20}$  two complex rays pass one of which does not belong to  $\Omega^{20}$ , in the case under discussion the last ray coincides with the former, so that it might look as if here a torsal line of the third kind was generated; but it would have to be possible to show that in the plane through  $l$  and such a line only twelve other generatrices of  $\Omega^{20}$  were situated, or that whilst tending to such a plane two generatrices were tending to each other, for which there is no reason whatever; so we conclude that  $\Omega^{20}$  does not possess torsal lines of the third kind, and we shall find this conclusion justified in future in different moments.

16. In a plane  $\lambda$  through  $l$  lie fourteen generatrices of  $\Omega^{20}$ ; through each of the points  $L$  in which these generatrices intersect  $l$  five other generatrices pass which in general determine with  $l$  70 different planes; we shall conjugate these to  $\lambda$ . In this manner the planes through  $l$  are arranged in a symmetrical correspondence of order 70; we wish to submit the 140 double planes  $\sigma$  of this correspondence to a closer investigation. Such a plane is evidently generated if for a certain point  $L$  of  $l$  two of the 6 generatrices  $s$  through that point lie with  $l$  in the same plane; the point  $L$  is then evidently at the same time a point of the nodal curve of  $\Omega^{20}$  lying on  $l$ , for this double curve is the locus of the points of intersection of all generatrices lying in a plane  $\lambda$  through  $l$ . We shall now, however, show that each suchlike plane as a matter of fact represents two coinciding double planes. Let us assume to that end a plane  $\lambda$  in which two generatrices  $s_1, s_2$  are lying, cutting  $l$  in two points  $L_1, L_2$  lying close together. Through each of these last pass five generatrices not lying in  $\lambda$ , and that in such a way that one of the generatrices through  $L_1$  lies in the vicinity of  $s_2$  and inversely, whilst the remaining ones lie two by two in each other's vicinity. If we allow  $\lambda$  to transform itself gradually into  $\sigma$ , then that one generatrix through  $L_1$  coincides with  $s_2$ , and inversely, whilst the remaining ones coincide two by two in four double planes of the second kind

to which  $\sigma$  corresponds as "branch plane" <sup>1)</sup>; if we remember that in  $\sigma$ , besides  $s_1$  and  $s_2$ , lie only twelve other generatrices of  $\Omega^{20}$ , then to  $\sigma$  are conjugated  $12 \times 5 + 2 \times 4 = 68$  planes not coinciding with  $\sigma$ . The two missing ones do coincide with  $\sigma$ , so that  $\sigma$  is really a double double plane.

It is easy to see that the reasoning given here is literally applicable to the six double generatrices, but not to the torsal lines of the first kind, and much less to those of the second. The plane  $\lambda$  through a torsal line of the first kind is, it is true, a double plane  $\sigma$ , but only a single one, for besides that torsal line there are now in  $\sigma$  still 13 other generatrices of  $\Omega^{20}$  (because namely the torsal plane does not pass through  $l$ ), and through the pinchpoint pass four generatrices not lying in  $\sigma$ ; so to  $\sigma$  are now conjugated  $13 \times 5 + 4 = 69$  planes, so that only one coincides with  $\sigma$ . And as for the torsal lines of the second kind, these give no rise whatever to double planes, but only to branch planes. Let us assume again, as above, a plane  $\lambda$ , in which lie two generatrices  $s_1, s_2$  which almost coincide, but in such a way, that their point of intersection lies at finite distance from  $l$ . Through  $L_1$  and  $L_2$  pass again every time five generatrices not lying in  $\lambda$ , but now lying neither in the vicinity of  $s_1$  nor of  $s_2$ , and when  $\lambda$  transforms itself into the plane through  $l$  and the torsal line of the second kind, those ten generatrices coincide two by two; so the torsal plane becomes a fivefold branch plane, but not a double plane.

Let us now draw the conclusion from these considerations. If we assume the double curve of  $\Omega^{20}$  to have  $x$  points in common with  $l$ , then our correspondence contains  $x + 6$  (namely on account of the double generatrices) double planes counting twice, and 48 (on account of the torsal lines of the first kind, see § 14) double planes counting once, so that the equation exists:

$$2(x + 6) + 48 = 140$$

out of which we find:  $x = 40$ .

So the double curve of  $\Omega^{20}$  rests in 40 points on  $l$  and is therefore of order  $40 + 91 = 131$ .

A plane section of  $\Omega^{20}$  contains however not only 131 double points, but  $131 + 6 + 15 = 152$ , viz. 6 on the generatrices and a sixfold point on  $l$ ; so it is of class  $20 \times 19 - 2 \times 152 = 76$ , so that if we again apply the formula

$$\varepsilon \sigma = 2 \cdot \varepsilon \beta - 2 \cdot \varepsilon g$$

we must substitute for  $\varepsilon \beta$  the number 76; and as  $\varepsilon g = 20$ , because the line of the condition  $g$  intersects  $\Omega^{20}$  in 20 points, we find.

<sup>1)</sup> EM. WEYR, "Beiträge zur Curvenlehre," pp. 9, 10.

$$\varepsilon \sigma = 2 \cdot 76 - 2 \cdot 20 = 112.$$

This number comprises all pairs of lines of the surface whose components lie at infinitesimal distance and intersect each other, thus the 6 double generatrices, the 48 torsal lines of the first kind and the still unknown number of torsal lines of the second kind: so  $\Omega^{20}$  contains 58 torsal lines of the second kind.

For a congruence is characteristic, besides the number of rays through a point (in our case 6) and in a plane (in our case 15), the number of pairs of rays which belong with an arbitrary line to a pencil, the so-called rank; according to the preceding this number is nothing but our quantity  $x$ , thus 40; the congruence deduced from  $\Omega^{20}$  is therefore a (6, 14, 40).

The results found above allow being controlled, by our finding the  $4 \times 131 = 524$  points of intersection of the surface  $\Omega^4$  with the nodal curve of  $\Omega^{20}$ . The greatest number of these points we find united in the points  $T_i$  and  $T_i^*$ , the eight nodal points of  $\Omega^4$ . A point  $T_i$  is a 36-fold point of the nodal curve (§ 13) and counts thus for 72 points of intersection; a point  $T_i^*$  is a tenfold point of the curve and counts thus for 20 points of intersection, together  $4 \times 92 = 368$ . In the 40 points where the nodal curve rests on  $l$ , the curve meets the double line of  $\Omega^4$ ; so this gives 80 points. In a pinch point of a torsal line of the second kind the nodal curve traverses  $\Omega^4$  in a single point of intersection. Let us assume e.g. a plane  $\lambda$  through  $l$  and such a torsal line as well as two planes  $\lambda_1$  and  $\lambda_2$  on both sides of  $\lambda$  and in the immediate vicinity of  $\lambda$ ; then in  $\lambda_1$  e.g. two generatrices of  $\Omega^{20}$  will nearly coincide, so their point of intersection will almost lie on the conic of  $\Omega^4$  lying in this plane; in  $\lambda$  itself this point of intersection really falls exactly on  $k^2$ , and in  $\lambda_2$  the two tangents have become conjugate imaginary; their point of intersection has nevertheless remained real, i. e. the nodal curve naturally continues its course but now lies inside  $k^2$ ; so it has intersected the surface. As  $\Omega^{20}$  possesses 58 torsal lines of the second kind we find 58 new points of intersection.

We must finally discuss the 6 double generatrices of  $\Omega^{20}$  which bear themselves as regards the nodal curve about the same as torsal lines of the second kind do. We must not lose sight of the fact that a double edge  $d$  of  $\Omega^{20}$  is a singular ray for the congruence but not for the complex; so if it intersects  $l$  in  $D$ , then the complex cone of  $D$  shows in no way anything particular; the plane  $\lambda$  through  $l$  and  $d$  contains thus two different generatrices of that cone, of which  $d$  is one. The consequence is that the conic of  $\Omega^4$  in  $\lambda$  must touch the line  $d$  in some point or other not lying on  $l$ , through

which point the nodal curve passes, just as with a torsal line of the second kind; and indeed the plane  $\lambda$  through  $d$  contains besides  $d$  only twelve generatrices of  $\Omega^{20}$ , intersecting each other mutually in  $\frac{1}{2} \cdot 12 \cdot 11 = 66$ , and  $d$  in 12 points counting double, which amounts together to  $66 + 24 = 90$  points of the nodal curve; so one is missing, but is the point of intersection in a closer sense of the two generatrices coinciding in  $d$ , and according to the above this cannot lie on  $l$ . In passing we learn from this consideration that *the nodal curve of  $\Omega^{20}$  touches each plane through  $l$  and either a torsal line of the second kind or a double edge in twelve points lying either on that torsal line or on that double edge.*

That a double edge, however, does not bear itself altogether as a torsal line follows from a repetition of the above given consideration with the three planes  $\lambda_1, \lambda, \lambda_2$ ; for now in  $\lambda_1$  as well as in  $\lambda_2$  two *real* generatrices of  $\Omega^{20}$  will lie. Nevertheless the nodal curve has here with  $\Omega^4$  not only a contact by two points, but even one by three points, so that the plane of osculation of the nodal curve coincides with the tangential plane of  $\Omega^4$ , and the nodal curve touches one of the two branches of the section of  $\Omega^4$  lying in the tangential plane.

Indeed, it is clear that besides the  $368 + 80 + 58 = 506$  points of intersection already found no others are possible than the 6 points on the double edges, which occupy us here; for each point of intersection not lying on  $l$  must be the point of contact of a generatrix of  $\Omega^{20}$  with a conic of  $\Omega^4$ , so a pinchpoint of a torsal line of the second kind, or of a double edge; as there are 6 of the latter sort in evidence and  $524 - 506 = 18$  points missing, each of those six points must be counted three times.

**Physiology.** — “*The posterior longitudinal fascicle, and the manege movement.*” By Dr. L. J. J. MUSKENS. (Communicated by Prof. C. WINKLER).

(Communicated in the meeting of October 26, 1912).

In a series of experiments in cats by means of different needles a lesion was caused in the cerebro-spinal axis, between the posterior commissure and the vestibular nuclei, avoiding the *N*-vestibularis, of which the lesion invariably causes such vehement rolling movements to the side of lesion, that the observation of the manege-movements is impossible. The microscopical control of the lesion and its results was performed after the method of MARCHI.

In three cases both posterior longitudinal fascicles were cut. Without exception the posterior longitudinal bundles were found degenerated, as well above as below the lesion, but not always equally heavily. Especially to the oral side the number of strongly stained fibres rapidly diminishes, reminding of GEE and TOOTH's observation <sup>1)</sup>, which particularly strikes one in 114, where within the domain of the oculomotor nuclei the lesion was performed. As well the ascending as the descending degeneration involves in these cases the whole area of the longitudinal bundle.

The physiological result is naturally different, according to the additional lesion of the cerebral stem. The spontaneous locomotion is always seriously interfered with. Forced movement, in the form of manege-movement, is as a rule absent and the stature of these animals answers to the description of the attitude after extirpation of both labyrinths. Only in case 90 as an exception manege-movement to the right was observed, which in this case should be attributed to the fact, that a bloodextravasation had happened at the cross-section of the left longitudinal bundle, which had caused during some days an asymmetrical irritation. This is inferred from the results after unilateral section of the longitudinal bundles.

In a second series of experiments a unilateral lesion of the longitudinal bundle was applied, with little or no lesion of the DEITERS Complex. In these three cases regularly an ascendent degeneration of the lateral part, especially of the severed longitudinal bundle was observed. Downward equally degeneration in the middle part of the cross section of the bundle was found, whereas also on the other side in the same field some degeneration was noted. Equally regularly in these cases *manege-movement to the side of the non-sectioned longitudinal posterior bundle* was observed during life; solely on 111 also the allied symptom of conjugated deviation of head and eyes was noted.

In a third group a unilateral lesion of the DEITERS Complex was caused. In this series of animals the results were neither anatomically, nor physiologically so easy to understand as in the two first groups. Regarding the degenerated fibres in the posterior bundle, they are in all cases far less numerous, compared with direct lesion of the bundle; also here it holds good more than for group 2, that degeneration, limited on one side only, is a rare occurrence; but in all cases very decided predominance of the degeneration on one side was found. Of these (7) animals in one (158) a total longitudinal lesion was performed *at the left side of the left longitudinal fascicle,*

<sup>1)</sup> Brain 1898.

in such a way, that all fibres from the left DEITERS Complex towards the posterior bundles and the raphe, had been cut leaving the left longitudinal bundle practically intact. Solely in this animal both longitudinal fascicles were upward degenerated, on the right side more heavily than on the left side. In three animals the lesion struck the DEITERS nucleus (118, 113 and 99). In these cases in the contra lateral longitudinal bundle a limited degeneration was found. In three animals (95, 93 and 111) the most proximal-dorsal cell group of the vestibular-complex (BECHTEREW's Nucleus) was struck; in this series a very limited degeneration on the side of the lesion in the lateral part of the bundle, rather mixing with the fibres of the fasc. DEITERS ascendens (WINKLER<sup>1</sup>), could be followed up. All these ascendent degenerated (more medially in the areal of the longitudinal bundle after lesion of DEITERS nucleus, more laterally after lesion of BECHTEREW's nucleus) fibres can be followed up to the oculomotor nuclei, where as in all cases, some strands of fibres could be traced up to the nucleus of the posterior commissure. The descending degeneration after lesion of the DEITERS complex is usually not very extensive, but present on both sides, regularly stronger on the side, where there is more marked *ascending* degeneration.<sup>2</sup>) These fibres occupy, lower down, more and more a ventral situation and can be traced down to the cervical medulla and lower down. For reason of comparison one of PROBST's experiments<sup>3</sup>) has been added to the table.

The degeneration found in these cases seems to prove, that solely for the distal nuclei of the vestibular complex (especially the triangular part) FUSE's dictum holds good, that the structural connection between the DEITERS-complex and the longitudinal bundle is a crossed one. Here the results, obtained by GUDDEN's method, are reinforced by those of MARCHI's method. On the other hand with the latter method it appears hardly subject to doubt, that the connection between BECHTEREW's nucleus and the longitudinal bundle is mainly a homo-lateral one, these fibres mixing with the fasc. DEITERS ascendens.

Regarding the phenomena observed during life, it is surprising that, equally regularly as in group 2 manege-movement was observed to the non-sectioned side, equally regularly also in these animals

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1) Central Course of the nervus octavus. Verhandelingen der Koninklijke Akademie van Wetenschappen. Tweede sectie 1907.

2) This detail seems to be able to support RAMON Y CAJAL's and MONAKOWS contention, that the fibres from the DEITERS-complex to the posterior longitudinal fascicles all split up in an ascending and descending branch.

3) Jahrbücher f. Psychiatrie 1901. P. 7 of the separate paper.

manege-movement was noted to the side where the P. L. B. shows the least degeneration (the lesion being on the same or on the other side). Some reserve I have to make here for the homo-lateral degeneration in the longitudinal bundle after lesion of BECHTEREW'S nucleus. For in 95, being the animal, that produced the most classical circus-movements to the left, a very local lesion was found in the middle part of the ingoing fascicles of the N. vestibularis. It can a priori not be excluded, that such a direct and local lesion of the nerve may cause manege-movement to the other side, in the same way as *usually* any lesion of the vestibular nerve causes vehement and long lasting rolling movements to side of the lesion<sup>1)</sup>. Such an interpretation seems however very improbable indeed. As to 111, the lesion was here accompanied by an haemorrhage and rather extensive. The physiological analysis of the DEITERS-complex can go, I think, a little further, in that a lesion of the caudal part of the complex, e.g. on the right side, as well as a lesion of the proximo-dorsal part (BECHTEREW'S nucleus) of the left side resulted in an ascendent degeneration in the P. L. B., of the left side, and also produced equally circusmovements to the right. This circus movement to the right side being elicited from an anatomical entity on either side, we are led to believe, that a double sided connexion of either horizontal semicircular canal with DEITERS nucleus and a proper extension of EWALDS experiments might clear up this point.

From these results I think it must be admitted, that the physiological function of the P. L. B., or at least one of its functions, is intimately related to the coordinated locomotion in the horizontal plane of eyes, head, trunk and extremities. A similar suggestion of such a relation is often found in literature, but about the precise form and direction resulting from such coordination none of these researches give information (EDINGER)<sup>2)</sup>.

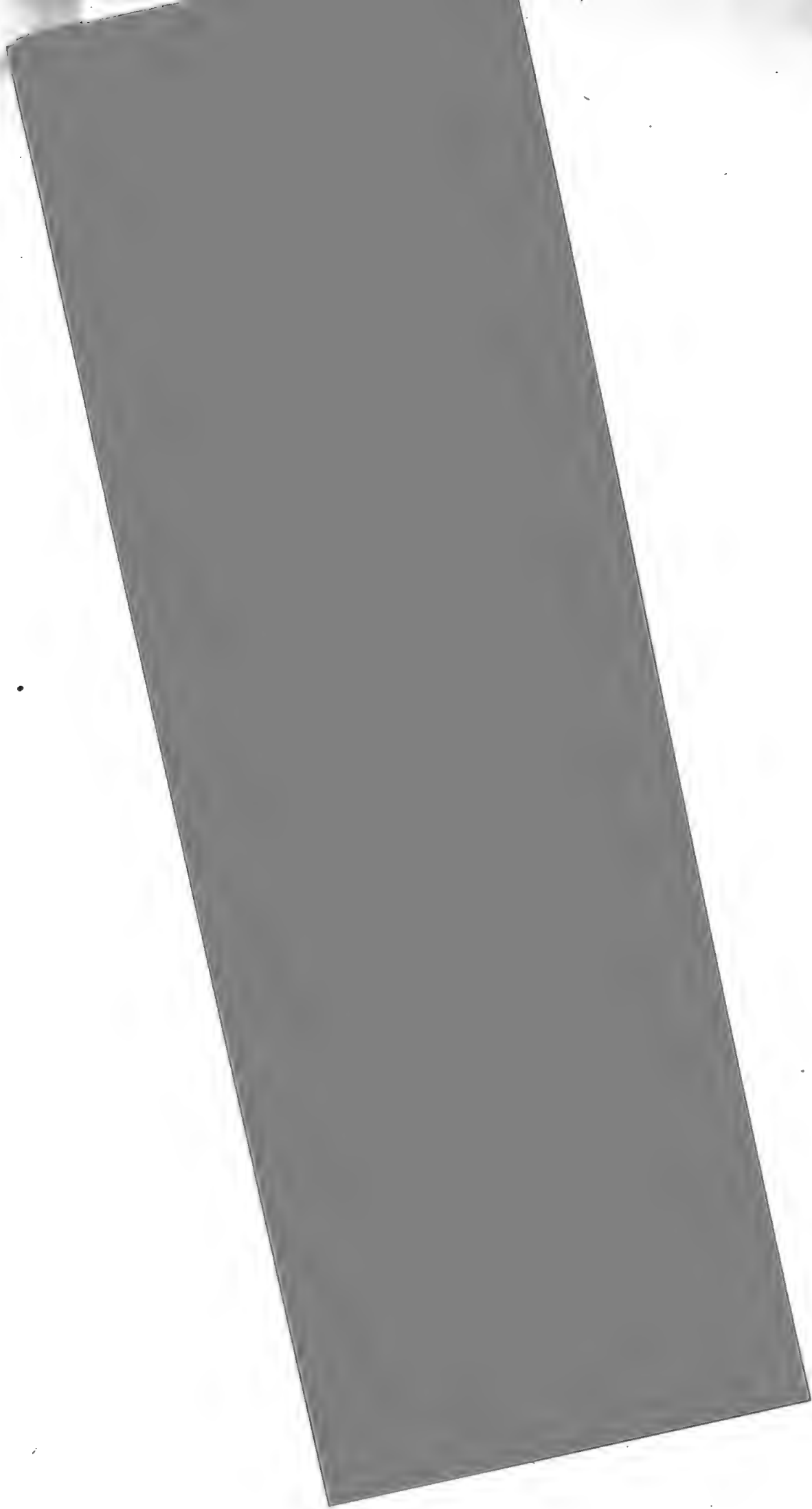
In a fourth group of experiments (in 6 animals) a lesion was applied in the region of the corpora quadrigemina anteriora, of the commissura posterior and of the red nuclei. In four cases descending degeneration from that region into the posterior longitudinal bundle, exclusively on the side of lesion, was found. This degeneration, sometimes amounting to no more than a few fibres, is lost sight of high in the medulla oblongata, especially in the region of the abducens-nuclei. In 2 of these cases accurately the origin can be followed in the series and it appears that the nucleus of the posterior commissure is involved

1) Compare: Studies on the forced movements. Journal of Physiology. XXXI. Ne. 3 and 4. 1904.

2) Vorlesungen. 1912, P. 110.



		<i>Descending degeneration of P. L. B. (distally to the lesion)</i>	
Group	ion	Left	Right
I		Total, lower down (in medulla) ventro-med. Total lower down ventro-medial	Total, lower down (in medulla) ventro-med. Total, lower down ventro-medial
	ays	Total, lower down ventral	Strong and complete, lower: ventral
II	"	Little	Ventro-medial part (to lumbar region)
	"	Total, lower down ventro-medial	A few fibres
	"	Tot., median part esp.	Moderate
	"	0	Degeneration
III	"	Lateral part (strong)	Medial part, rather diffuse
	ay	Medio-ventral (till dorsal region)	Lateral (+F. Deit asc.)
	ays	"	"
	"	0	Few fibres (med.), to dors. part of medulla
	"	0	Latero-ventral, to cervical region
	"	0	Little, lateral, to low in medulla spinalis
IV	"	Latero-ventral	Few fibres
	"		Medio-dors. (not lower than striae acust.) Few fibres
	"		Fasc. interstitialo-spinalis
	day		Few fibres
	"		Very little
V	days	Well degenerated (to medulla oblongata; there more ventral)	Little (medial), to medulla; there more ventral)
	"	0	0
	"	0	0
	"	Some fibres to exit of N. Trigemini	



in the region of the direct lesion or of the local malacy. My supposition that this nucleus must be regarded as the origin of this commissuro-medullary bundle, gains in probability by the findings in 2 cases (106 and 108), where this bundle was not degenerated. In 106 the lesion involves exclusively the superficial layers of the anterior corpus quadrigeminum, but leaves the nucleus of the commissure intact. In 108 an extensive sagittal lesion in that region was found. Here from the surroundings of the red nucleus a strand of degenerated fibres can be followed in the homolateral posterior bundle, which however does not disappear at the level of the n. abducens, but can be traced far lower down, as far as in the dorsal spinal cord. Probably we deal here with the homolateral tecto-spinal bundle of PROBST.

As to the forced movements, it is remarkable, that all these four animals with the degeneration of the commissuro-medullary bundle performed circus-movements for a short period to the side of the lesion, whereas the animal with lesion in the corpus quadrigeminum anterius solely, and that with lesion of the nuc. ruber exclusively did not do so.

In relation with these cases we have to mention two animals with extensive lesion of the *cerebral hemisphere*. Whereas in 127 solely an extensive extirpation of the anterior pole was performed, leaving the thalamus opticus intact, in 186 the whole hemisphere was extirpated and also the thalamus wounded. Only in this latter animal on the operated side some degenerated fibres were found, of which the course is exactly that of our commissuro-medullary bundle. This latter animal showed decidedly circus-movements *to the operated side* during some days.

From these results we conclude, in agreement with current anatomical notions, that the posterior longitudinal bundle contains fascicles of different source and end-station. At any rate in the medial portion of the P. L. B.-formation 3 bundles must be distinguished, two *ascendent* and a *descendent* one dealing with the coordinated locomotion in the horizontal plane. Innermost within the medial portion of the P. L. B. we find the descending commissuro-medullary bundle; next comes the crossed ascendent DEITERS P. L. B.-bundle, then comes the homolateral BECHTEREW-P. L. B. bundle, containing fewer fibres than the crossed one. The latter bundle lies entirely within WINKLER'S Fasc. DEITERS ascendens. In a next paper the physiological analysis of the rest of the P. L. B. formation will be dealt with. There are many preparations in my collection, which tend to prove (as far as MARCHI-work is entitled to do so), that, as is suggested by the authors, the vestibular-P. L. B. fibres, as well the crossed as the homolateral ones, in the

P. L. B. formation bifurcate, one limb ascending to the oculomotor nuclei and the nuc. of the posterior commissure, the other passing down to the cord.

The descending bundle has its origin exclusively, so it appears, in the nuc. commissurae posterioris (VAN GEHUCHTEN, PROBST) and can be traced as far as the homolateral abducens nucleus. The oral and distal final stations of both coordinating bundles are therefore found in the same level, a detail which seems particularly inviting to study here the physiology of the bundle as a common final path (SHERINGTON). For the study of the mechanism of the circus and rolling-movements undoubtedly labyrinth- and neck-reflexes described by MAGNUS and DR. KLEYN<sup>1)</sup> as well as BARANYI'S experiments<sup>2)</sup> have to be considered.

As to the function it can be hardly considered accidental, that in my experiments the animals with ascending degeneration in the P. L. B., on one side (e.g. on the right side) performed circus-movement to the other side, to the left; whereas the animals with a (from the Nuc. comm. post) descending degeneration e.g. on the right side, did their manege-movements to the diseased side. PROBST'S law<sup>3)</sup> that "a hemisection of the brainstem anterior to the red nuc. caused manege-movements to the diseased side; a hemisection caudal to the red nucleus to the healthy side", seems therefore, well founded, but with this important restriction, that the nuc. commissurae posterioris and not the red nuc. is the origin of the commissuro-medullary bundle, and that not hemisection, but a simple lesion of one longitudinal bundle will suffice, to cause the circusmovements.

By comparison with a number of other series and subtraction of the phenomena during life, it can be proved, that lesion of the great descending tracts (pyramidal, rubro-spinal, tecto-bulbar, vestibulospinal, and ponto-spinal tracts), of the most important ascending systems (GOWERS'S and FLECHSIG'S tract) the lemniscus and cerebello-rubral tracts have nothing to do with this function. I am not in a condition to deny nor to affirm CLARKE and HORSLEY'S supposition<sup>4)</sup>, that the ponto-cerebellar connections should have to do with the "mouvement de manege" but I do think as long as there is no proof forthcoming, regarding a centre for equilibration in the temporal lobes, that after these experiments there is no need to fall back upon any such conjecture.

<sup>1)</sup> Archiv. f. d. gesammte physiologie, 1912. Bd. 145. S. 455.

<sup>2)</sup> Neurologischer Centrallblatt. 1912.

<sup>3)</sup> Loc. cit. p. 41.

<sup>4)</sup> Brain 1905

In the course of these experiments, having specially in view the posterior longitudinal bundle and the DEITERS-complex, it appeared, that — at least for this system — in relation to the disturbances observed during life one has to distinguish three different modes of traumatic lesion. 1. Total destruction of a cell-complex or bundle through the instrument used, with renders the structure irrecoznizable, the tissue being totally or partly replaced by a moderate bloodextravasation. After this lesion invariably a total degeneration of all fibres arising from or passing this region occurs, if care be taken, that the specimen does not stay too long in MULLERS fluid. 2. Malacy of a region which causes in a selective way some systems of fibres to degenerate, whereas other systems apparently continue to be nourished and probably also continue their function <sup>1)</sup>. In view of KOHNSTAMM'S and MONAKOW'S findings it appears, as if the great, the middle-sized and the small cells of the DEITERS-complex suffered unequally in their nourishment, if this structure happens to be involved in such a malacy. 3. If an extensive haemorrhage occurs and exerts compression, irritative symptoms appear of the same order <sup>2)</sup> but more vehement, than those which are caused by the dissolution of the medullary sheath and the moderate irritation, caused by this process.

In judging about the physiological consequences, it must be kept in view, that every lesion after 1. and 3. is always found surrounded by a zone of malacy, and finally, that in a case with voluminous haemorrhage in the brainstem the general brain-compression may mask completely the forced movements.

It is quite natural, that in different experiments the vestibular P. L. B.-complex was repeatedly wounded on more than one locality. Regarding the physiological effect it appeared, that a lesion of the N. vestibularis itself predominates above a lesion of its nucleus, and the latter again dominates above a lesion of the posterior longitudinal bundle.

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<sup>1)</sup> So I found in 102, that the left longitudinal bundle passed such a malacy in the upper pontine region. The descending commissuro-medullary bundle was degenerated and the animal had shown the physiological consequence of this degeneration; the ascending vestibular-P. L. B. fibres were not degenerated.

<sup>2)</sup> It is interesting to note, regarding the nucleus of the posterior commissure, that after E. SACHS' experiments (Brain 1909, p. 180) direct electrical stimulation of this region causes conjugated deviation to the opposite side; which evidently corresponds to the effect, described in this paper, of the stimulation exerted on the nucleus of the posterior commissure by the degeneration of a number of ascending fibres, running in the P. L. B. and ultimately arriving in this nucleus. The circus movement in many of my experiments was accompanied by conjugated deviation to the same side; both phenomena evidently being narrowly related.

**Geology.** — “*On the formation of primary parallel-structure in lujaurites.*” By Dr. H. A. BROUWER. (Communicated by Prof. G. A. F. MOLENGRAAFF).

(Communicated in the meeting of October 26, 1912).

In an important memoir of the late Professor N. V. USSING<sup>1)</sup> we find a detailed discussion on the question of the origin of schistose structure in lujaurites. It is explained as a consequence of fluctuation, in contradiction to RAMSAY'S<sup>2)</sup> view, who admits a slow cooling and undisturbed crystallization of the magma for the rocks of the peninsula of Kola.

In my description of the Transvaal nepheline-syenites<sup>3)</sup> the name lujaurite was extended to rocks without parallel-structure, characterized by the occurrence of fine-needle-shaped crystals of aegirine in abundance. The parallel-structure where it occurs was explained as a consequence of a crystallization influenced by one-sided pressure, which view will be now more explicitly explained.

*Geological connection with accompanying rocks.*

In the peninsula of Kola no remains of the roof of the intruded batholite have been preserved and thus it is not certain whether the lujaurites are the first products of consolidation in the marginal zone of the igneous mass. In the Pilandsbergen (Transvaal) the schistose varieties are often still surrounded by a border of nepheline-syenitic or syenitic rocks, whilst in the Greenland intrusions which have been very carefully examined, the lujaurites form the lowermost rocks of a stratified batholite which has been denuded. The last mentioned rocks are covered by a very coarse-grained foyaitic rock (naujaite) the crystals of which are sometimes a few decimeters large; it is characterized by sodalite poikilitically surrounded by all other minerals. Pegmatitic segregations are found chiefly in a horizontal position, whilst in the rock itself a more or less horizontal stratification in thick layers is indicated. Towards the upper portion the naujaite gradually passes into a sodalite-foyaite, whilst downwards it is connected with the underlying lujaurites by a brecciated zone of transition. This breccia-zone is formed by strata of lujau-

<sup>1)</sup> N. V. USSING, Geology of the country around Julianehaab, Greenland. Meddelelser om Gronland, vol. XXXVIII, and Muséum de Min. et de Géol. de l'Université de Copenhague, Communications Géologiques N<sup>o</sup>. 2, 1911.

<sup>2)</sup> W. RAMSAY, Das Nephelinsyenitgebiet auf der Halbinsel Kola, I and II. Fennia 11 and 15, N<sup>o</sup>. 2. Helsingfors 1894 and 1899.

<sup>3)</sup> H. A. BROUWER, Oorsprong en samenstelling der Transvaalsche nephelien-syenieten. 's Gravenhage, MOUTON & Co, 1910.

rite entirely surrounding the lenses of naujaite and increasing in number towards the bottom, so that a structure is formed which reminds of the "Augenstruktur" of some gneisses if this were thought many times magnified. Commonly the lujaurites of the breccia-zone are black (arfvedsonite-lujaurites), but occasionally — and this is of importance for the genesis — we find also green aegirine-lujaurite, bounded on either side by black arfvedsonite-lujaurite, thus proving that differentiation has taken place.

The rocks of the lujaurite-complex of Greenland, which is more than 600 m. thick, are, as a rule, more fine-grained than those of Kola and Transvaal and contain a greater quantity of dark constituents. Complexes of kakortokites alternate with the lujaurites; these are foyaitic rocks, distinguishing themselves from the normal foyaites by a greater percentage of dark minerals; they are more coarse-grained than the lujaurites, and their average composition corresponds pretty well with that of the latter. Light-coloured, red and dark strata alternate, and it is peculiar that the same succession constantly returns, and, in the thickest parts of the complex, repeats itself about forty times. As in the breccia-zone of the lujaurites, the kakortokites likewise envelop fragments of naujaite.

The above-mentioned variations originating from the same parent magma are likewise met with among the Transvaal rocks; their mutual connection here, however, is more irregular, and can less clearly be observed in the field because they are in most places covered by other rocks.

#### *Mechanism of the intrusion of the Pilandsbergen.*

It is peculiar that in the territory of the Pilandsbergen effusive rocks are found in large quantity between the deep-seated<sup>1)</sup> whereas they do not occur in the surrounding granites and norites.

It is very likely that, in the Pilandsbergen and its environs originally a roof of volcanic rocks has covered the deep-seated rocks, because elsewhere in the igneous complex of the Boschveld a thick volcanic series still forms the roof of the deep-seated rocks, which is intersected by dykes of tinguaitic and camptonitic rocks<sup>2)</sup>. In connection with the intrusion of the foyaitic magma which is younger than both the granites and norites, the roof has locally sunk

<sup>1)</sup> H. A. BROUWER, loc. cit. p. 16.

<sup>2)</sup> H. A. BROUWER, loc. cit. p. 35 and 89.

P. A. WAGNER, Note on an interesting dyke intrusion in the upper Waterberg system. Transactions Geol. Soc. of South Africa 1912, p. 26 sqq.

down, and whilst it has disappeared everywhere else in the neighbourhood by erosion, we see the remains preserved just on these spots where the roof has given way.

Consequently the massive of the Pilandsbergen does not belong to that important class of intrusions, to which tangential pressure in the portion of the earthcrust in which the intrusion takes place is necessarily connected, which is proved moreover by the existence of a great number of vertical dykes of vast extension. Blocks sinking elsewhere cannot have been the cause of the intrusion of the magma, as the roof has sunk down exactly on those spots, where the foyaitic magma has risen. Certainly pressure and faults are directly connected with the mechanism of the older chief intrusion of the Boschveld<sup>1)</sup>, and also the young foyaitic intrusions are chiefly restricted to those spots where tension has taken place, and consequently the pressure has been diminished.

Thus both the sinking down of the roof and the intrusion are regarded as consequences of the same common cause, which occasioned the relief of pressure; the question in how far the sinking down of fragments of the roof into the magma underneath has contributed to the batholitic invasion (DALY'S "overhead stoping") is in this respect of secondary importance; we must however admit that sinking down and intrusion took place partly simultaneously.

Similar conditions are found likewise in the Greenland rocks.

#### *Formation of the schistose structures.*

The formation of these structures in consequence of flow in the crystallizing magma is improbable for the following reasons:

1. *For a great vertical distance the direction of the plane of schistosity by parallel-structure remains the same.* Consequently we should have to admit in a batholite for a considerable height a gradual decrease of rapidity in the flowing magma. RAMSAY has already pointed out the improbability of this theory.

2. *The aegirine-needles lie for the greater part parallel to the plan of schistosity but in it they are irregularly distributed.* In a flowing magma the needles would have a tendency to arrange themselves parallel to the direction of the flow. Indications of such an arrangement are missing.

3. *The lujaurites vary and by transitions are connected with other rocks without parallel structure.* If we admit flow-structure, then other

<sup>1)</sup> G. A. F. MOLENGRAAFF, Geology of the Transvaal. Johannesburg 1904, p. 50 sqq. A. L. HALL, Ueber die Kontaktmetamorphose an dem Transvaalsystem im östlichen und zentralen Transvaal. Min. u. Petr. Mitt. XXVIII, Heft 1, 2, 1909.



rocks being crystallized almost simultaneously as well above as below with the lujaurites, likewise ought to show a parallel structure.

4. *In the breccia-zone between the Greenland lujaurites and the naujaites differentiation towards the marginal zones occurs.* As the lujaurites between the naujaite-blocks distinguish themselves from the others only by the fact that the parallel arrangement of the composing minerals follows planes which bend round the naujaite-blocks, a continual current ought necessarily to have taken place also between the naujaite-blocks, which would have prevented the differentiation.

An other explanation for the strongly varying structures we have described will now be suggested.

The parent magma of all these rocks is characterized by a high percentage of pneumatolytic gases and connected with it a strong power of crystallization and a thin fluidity maintained to a comparatively low temperature. As the different foyaitic rocks of Greenland and most likely also those of the Pilandsbergen have crystallized with only very slight differences in time, the temperature can only be a secondary factor in the mode of formation of these greatly varying structures. The differentiations caused by fractional crystallization or by separation according to the specific gravity may likewise be left out of account, as they modify chiefly the composition and not in the first place the structure of the rocks.

From such a magma coarse granular varieties will be formed under undisturbed conditions of crystallization, whilst poikilitic structures can be explained by differences in power of crystallization, in connection with affinity and with the relations between the quantities and the solubilities of the components. For the fine granular varieties a rapid mode of crystallization is essential, but movements in the magma are not required. This rapid crystallization can be caused by the escape of gases from the magma which remained thin fluid down to a low temperature on account of the great percentage of pneumatolytic gases kept in solution, whereas by the escape of the gases it suddenly becomes viscous, so that large crystals cannot develop themselves any more.

If now during the crystallization a one-sided pressure prevails, this pressure — transformed in the thin fluid magma into an all-sided one — will be able to make its influence felt. Consequently it is not accidental that exactly the fine-granular lujaurites show a great inclination to parallel-structure. *In the viscous magma no strong currents can take place; no parallel structure can thus be formed in it.* In case larger feldsparcrystals had already been formed before

the relief from pressure, they will be placed parallel one to the other and be surrounded by a felt of aegirine-needles (Kolarocks); in case no one-sided pressure prevails, a rock will be formed distinguishing itself from the normal foyaïtes by the habitus of aegirine and arfvedsonite.

The viscosity of the magma will check the escape of gases, and the gradual supply of gases from the underlying magma will occasion a transition into rocks of the habitus of the kakortokites, which are of an almost identical chemical composition and distinguish themselves from the lujaurites mainly by the increase of the size of the grains, by the absence of parallel-structure and by the needleshaped habitus of aegirine and arfvedsonite. The again increased pressure in this thin fluid magma is converted into a pressure from all sides.

The regularly returning succession of different variations of kakortokites was already explained by USSING by a periodically repeated relief of pressure assisted by separation according to the specific gravity. The appearance of narrow transition zones without deviating structure between the different variations, and the comparatively trifling thickness of the strata prove that the relief of pressure was less pronounced during the crystallization of the lujaurites.

The enclosing of the naujaite-fragments in the breccia-zone can be explained by a sinking of the roof, simultaneously with the decrease of volume and the crystallization of lujaurites, causing an increase of pressure which is favourable to the development of parallel-structure. During this process the parallel arrangement of the minerals will take place in planes which will bend round the naujaite blocks.

With a less regular sinking down of the roof, such as seems to have taken place in the Pilandsbergen, the pressure and the arrangement of the different structures in the batholite becomes likewise irregular. The successive periods of relief of pressure and the simultaneous escape of gases from the magma may have been accompanied by volcanic eruptions of varying intensity.

*Similarity in structures between the crystalline schists and the contactrocks.*

In rocks accompanying lujaurites, we find a great variety of sieve-structures which were discussed at large in a former communication<sup>1)</sup>.

Sieve- and parallel-structures are found also both in crystalline schists and contactrocks. This explains why travellers of the first half of the 19<sup>th</sup> century have mentioned chloriteschists and gneisses among the rocks of Greenland, and why CARL MAUCH<sup>2)</sup> enumerates

<sup>1)</sup> H. A. BROUWER, On peculiar sieve-structures in igneous rocks, rich in alcalies. These Proceedings XIV, p. 383.

<sup>2)</sup> C. MAUCH. Reisen in Süd-Afrika (1865—1872). Ergänzungsheft N<sup>o</sup>. 37 zu PETERMANN'S Geogr. Mittheilungen, p. 14, 1874.

gneisses among the rocks of the Pilandsbergen. This great similarity of structure points to analogy in the genesis; the principal factors for the formation of contactrocks are abundance of pneumatolytic gases, and crystallization at a low temperature, whilst recrystallisation under pressure in firm rock, as takes place in crystalline schists, will lead to a similar structure, as a sudden and rapid crystallization does under pressure in an already viscous magma, circumstances under which the normal laws ruling crystallization in a slowly cooling magma are no longer in force.

The varieties of lujaurite rich in aegirine or arfvedsonite, in which the feldspars are only developed as small crystals, show e. g. a great outward resemblance to some amphibolites. Characteristic of both of these is a simultaneous crystallization through the entire magma, or a simultaneous recrystallization through the entire rock, the consequence of which is the simultaneous formation of many little crystals. It will, however, generally be possible to distinguish between them, because in the igneous rocks with the habitus of crystalline schists the minerals that had already crystallized as phenocrysts under the influence of affinity, chemical equilibrium and relative solubility of the components, before the conditions of rapid crystallization set in, will continue to exist as such, whilst with the crystalline schists the entire preexisting mixture of minerals must adapt itself to the new circumstances and recrystallize at the same time, in consequence of which the formation of idiomorphic crystals is checked allthrough the rock, and this is also the case in the genesis of contactrocks. A greater molecular mobility however often still allows the development of idiomorphic crystals and of a succession of crystallizations in a cooling igneous magma. These differences can often distinctly be observed in the sieve-structures which are met with in both groups of rocks.

Defining the crystalline schists as metamorphic rocks, the lujaurites do not belong to this group; neither do many other rocks often regarded as crystalline schists. As such may be mentioned the rocks of numerous gneiss-areas situated outside large folded mountain-ranges which just as the above described nepheline-syenites show strongly varying types, whereas traces of dynamometamorphism after the consolidation are entirely wanting.

Finally the above mentioned facts and reasonings illustrate the importance of the agencies which are at work in the cases of piezocrystallization and piezocontactmetamorphism, with regard to the genesis of rocks of the habitus of the crystalline schists.

**Physiology.** — “*Form and function of the trunkdermatome tested by the strychnine-segmentzones*”<sup>1)</sup>. By J. J. H. M. KLESSENS. Communicated by Prof. WINKLER.

(Communicated in the meeting of October 26, 1912).

The theoretical trunkdermatome of man and mammals is a trapezium, the short basis of which lies in the dorsal diameter, and the long basis of which lies in the ventral diameter. This statement dates already from TURCK, who called the attention to the fact that dorsally a same number of posterior roots provides for the skin covering the thoracal-vertebrae, whilst ventrally they do so for a much larger part of the skin, extending from the manubrium sterni to the symphysis pubica.

It seems that the anatomically prepared dermatomes (BOLK<sup>2)</sup>, GROSSER and FRÖHLICH<sup>3)</sup>) support this view.

The root-fields experimentally fixed according to the “remaining aesthesia” method, that SHERRINGTON<sup>4)</sup> found with *Macacus rhesus*, have likewise a form answering to the theoretically postulated one. SHERRINGTON writes, that the string formed by the dermatomes on the trunk is, “somewhat wider near its ventral than at its dorsal end”. And passim: “each zone is narrowest at its dorsal end”. Yet SHERRINGTON remarks that the periphery of the dermatomes feels stronger than the central part, so that going from the border towards the centre for the fixation of sensibility, occasionally the sensibility suddenly appears to become much sharper.

A similar fact was stated for the dog by C. WINKLER and VAN RIJNBEEK<sup>5)</sup>. They saw namely that the sensible isolated zone generally deviated in extent and form from the theoretical dermatome. These

1) According to investigations made in the physiological laboratory of the University of Amsterdam.

2) L. BOLK, Die Segmentdifferenzirung des menschlichen Rumpfes und seiner Extremitäten. I—IV. Morphologisch Jahrbuch Bd. XXV. XXVI. XXVII. XXVIII. Leipzig 1897—1900 and: L. BOLK. Een en ander uit de segmentaal anatomie van het menschelijk lichaam. Ned. Tijds. v. Geneeskunde. Amsterdam. 1897. Vol. I. p. 982. Vol. II. p. 366.

3) O. GROSSER und A. FRÖHLICH. Beitr. z. Kenntniss der Dermatome der menschlichen Rumpfhaut. Morphol. Jahrb. XXX. S. 308. Leipzig 1902.

4) C. S. SHERRINGTON. Examination of the peripheral Distribution of the fibers of the posterior Roots of some spinal nerves I Transactions of the Royal Society of London. B. Vol. 184. p. 691. London. 1892.

5) C. WINKLER and G. VAN RIJNBEEK. On function and structure of the trunkdermatoma I—IV. Proc. of the K. Akademie van Wetenschappen te Amsterdam. 1902—1905. Amsterdam, and: C. WINKLER. Ueber die Rumpfermatome. Ein experimenteller Beitrag z. Lehre der Segmental-Innervation der Haut. Monatschr. f. Psychiatrie und Neurologie. Bd. XIII. S. 161. Berlin. 1903.

deviations were greater in proportion as the operative trauma for the investigation had been larger. Moreover they found a permanent regularity in the way in which the deviations presented themselves.

These facts brought them to the view that the isolated root-field that could experimentally be ascertained, can never have the entire extent of the theoretical dermatome. They supposed therefore that even in the most favourable experiments beyond the limits of the sensible zone, always another little strip of skin must be admitted as belonging to the dermatome. This strip they called "Marginal area", and pronounced i.a. the hypothesis which for the rest was no further elaborated, that this strip is not capable of independent sensation (i.e. without the assistance of the overlapping). This isolated sensible zone they called "central area". In the experiments of W. and v. R. the form and extent of this zone appeared to be extremely variable and dependent on the postoperative conditions of the isolated root and of the spinal cord. With a large operative trauma the form of the central area was no more than a "caricature" and its extent much smaller than might be expected from the dermatome. W. and v. R. call this part of the dermatome, that was found to be insensible likewise "marginal area". If we summarize W. and v. R.'s views, we find that even in the most favourable experimental isolations the zone that is found to be sensible does not constitute the whole theoretical dermatome, but only a central area of it shut in between two marginal zones that cannot be indicated. In unfavourable cases, when the central area becomes a caricature, the marginal area is widened at the expense of the central area.

In W. and v. R.'s experiments the latter phenomenon always occurred first and strongest in the ventral zone of the dermatome. As an explanation of the fact that the sensibility in the ventral zone appears to be feebler W. and v. R. adduce two hypotheses: 1<sup>st</sup> that the ventral part is the most excentric part of the dermatome (i.e. most distant from the C.Z.S. spinal cord and spinalganglion)<sup>1)</sup> and 2<sup>nd</sup> that on account of the "stretching" of the skin between manubrium sterni and symphysis the extremities of the nerves had to extend over a larger surface than in the dorsal zone.

On the occasion of a systematic examination of the strychnine-

<sup>1)</sup> Compare likewise: G. VAN RIJNBEEK. On the fact of sensible skin dying away in a centripetal direction Proc. of the K. Akademie v. Wetenschappen te Amsterdam 1903, and G. VAN RIJNBEEK. Beobachtungen über die Pigmentation der Haut bei Scyllium catulus und canicula und deren Zuordnung zu der segmentalen Hautinnervation dieser Thiere. PETRUS CAMPER. Nederl. Bijdragen tot de Anatomie. Dl. III. p. 137. Haarlem. 1904.

segmentzones of cats<sup>1)</sup>, of which I hope to make detailed communications on some subsequent occasion, I found some facts which, in connection with the questions mentioned above, I suppose to be of sufficient importance to be separately communicated here. My experiments are made on cats that by a high transverse section had been converted into spinal-cord animals. I apply then strychnine in the place where a root enters, and cut besides cranially two roots. Consequently I make use of a combination of the remaining aesthesia method and that of the local strychnine-poisoning of the spinal cord. I do so to be sure, that though there may perhaps exist some doubt about the decidedly local application of the poison, at all events, no stimuli of the skin can reach the spinal cord from roots situated beside those, of which I intend to fix the skin-zone.

By a slight touch of the skin with a pencil we look then further for hyperreflexion<sup>2)</sup>: usually this can already be shown a few minutes after the poisoning.

A peculiar fact that I have regularly stated at the determination and fixation of the zones, is that hyperreflexion appears first and strongest in a definite string-shaped zone, which however soon widens because cranially and caudally a strip of skin which at first was not hyperreflexory, becomes so now, though in an inferior degree to the zones that could first be indicated. When the entire strychnine-segmentzone has reached its largest extent, this difference of intensity still continues to exist, so that we can distinguish a central zone with stronger hyperreflexion from a narrower peripheric strip with less strong hyperreflexion.

This strychnine-segmentzone can consequently be divided into a strong hyperreflexory inner-zone which can soon be indicated, shut in by two feebler outer-zones appearing a little later.

These facts show an unmistakable correspondence with those mentioned above communicated partly by SHERRINGTON, partly by W. and v. R. I shall try to elucidate this peculiar behaviour of strychnine-segmentzones in connection with what has been found by the above-mentioned authors, chiefly on account of indications ascertained with a cat (marked 32) where, under specially favourable circumstances, successively three strychnine-segmentzones could be fixed, namely to the left Th. VIII and Th. XI to the right Th. VII.

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<sup>1)</sup> Compare J. G. DUSSER DE BARENNE. Die Strychninwirkung auf das Zentralnervensystem. I—IV. Folia Neurobiologica. Bd. IV. V. VI. Haarlem. 1910—1912.

<sup>2)</sup> With this form of strychnineapplication no Tetanus takes place, but only hyperreflexion.

1. *Strychnine-segmentzone Th. VIII left.*

After the cat had been made a spinal-cord-animal by a transverse-section at Thor. II a piece of thoracal spinal cord is laid bare in the usual way, and the place of introduction left of Th. VIII moistened with strychnine. Moreover the dorsal roots of Th. VI, VII, IX and X are cut intradurally. Soon it is possible to ascertain a strongly hyperreflectory zone of the skin, which gradually widens and a few minutes after the poisoning reaches its maximal extent. It is then still very easy to distinguish an inner-zone and two outer-zones.

a. *Description of the inner-zone.*

The central-zone is almost string-shaped. The cranial and caudal limits first run parallel to each other, perpendicular to the axis of the body. On the centre of the lateral surface the cranial limit makes however a curve convex to cranial. A similar phenomenon is scarcely indicated in the caudal limit.<sup>1)</sup>

The bordering lines continue to run parallel and perpendicular as far as the ventral surface. Here they converge slightly, so that the central zone that was at the d. d. 30 mm. wide, measures in the v. d. only 23 mm. The central zone however goes beyond the v. d. and finishes, sharply limited, about 4 mm. overlapping the crossed side. Here the hyperreflexion is somewhat slighter than in the rest of the zone. (A dorsal crossed overlap could not be fixed on account of the median skin-section).

The zone hitherto described is surrounded by a ventrally strongly widening outer-zone which being itself less reflectory than the inner-zone, contrasted however strongly with the adjoining areflectory resp. normally reflectory zone. The outer-limits of the outer-zone are of course at the same time the boundary of the total strychnine-segment-zone, which I am going to describe now.

b. *Description of the total strychnine-segmentzone (outer-limits of the outer-zone).*

Scarcely to be recognized at the d. d., running closely along the

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<sup>1)</sup> A similar fact is often indicated by W. and R. Compare e.g. their fig. 27 of their IIIrd communication. Here the 13th and 16th spinal roots were isolated. The caudal zone of the ventral part seems to be considerably shrunk, whilst cranially the lateral outward curve of the central area breaks through the anaesthetic zone. To explain these phenomena they admitted a widening of the central area in the lateral part, whilst at the same time it is supposed that here a relative minimum of sensibility is found. As now a similar removal of the border existed cranially and not caudally likewise with my cat, this fact may perhaps also be regarded as a peculiarity of the 16th root-field.

foremost limit of the inner-zone, the cranial limit of the total zone soon assumes a course directed more towards cranial, so that the cranial outer-zone, in the d. d. scarcely a few mm. wide, is in the v. d. 10 mm. wide.

The caudal boundary-line continues to run at the d. d. almost together with the caudal limit of the inner-zone; it is here hardly a few mm. to the outside. Its further course however is like that of the cranial limit strongly divergent, consequently here in a strong caudal direction, so that, especially in the ventral zone, a wide outer-zone appears, which in the v. d. is 21 mm. wide. The caudal outer-zone is consequently almost twice as wide as the cranial one.

If we regard now this large extent, and the shape that the total strychnine-segmentzone obtains by the addition of the so wide outer-zones, we should be inclined to admit that almost the whole theoretical, ideal dermatome has appeared here. If now we remember W. and v. R.'s conclusion:

“Isolirt man experimentell ein Dermatome so entspricht der erhaltene sensible Bezirk nie weder der Ausdehnung, noch der Gestalt nach, dem theoretischen oder anatomischen Dermatome,”<sup>1)</sup> then the combined strychnine-isolation method applied by me affords doubtless better results than the simple “remaining aesthesia method”. For under the influence of the strychnine poisoning the limited value for the reflexion diminishes so much that there can hardly anymore be question of a marginal area in the sense of W. and v. R.

## 2. *Strychnine-segment zone of Th. XI left.*

After the rootfield of Th. VIII had in this way been fixed and measured, the root Th. XI was isolated in the same way by cutting the dorsal roots of Th. XII and XIII, and locally poisoned with strychnine.

The hyperaesthetical zone that appeared here likewise, had a steep trapezium shape, and was when the total extent had been reached, at the d. d. 34 mm., at the v. d. 49 mm. wide. Here the cranial limit could however only be fixed, after the Th. VII, isolated in the preceding experiment, had been cut. For it appeared that the cranial limit of Th. XI crossed the caudal limit of Th. VIII in the level of its lateral cranial curve.

### a. *Description of the central zone.*

The central zone of Th. XI occupies dorsally also again almost

<sup>1)</sup> G. VAN RIJNBERK. Versuch einer Segmental-Anatomie. Ergebnisse der Anatomie. Bd. XVIII. Wiesbaden 1910. S. 544.



the total extent of the strychnine-segmentzone. Its limits have here likewise a parallel and perpendicular direction. On the lateral and ventral surface they assume also a distinctly converging course so that when they reach the ventral diameter, they are only 16 mm. distant from each other, whilst at the dorsal diameter the inner-zone is about 32 mm. wide.

b. *Description of the outer-limits of the outer-zone. (Total strychnine-segmentzone).*

The cranial limit lies in the dorsal zone, scarcely perceptibly cranially from the cranial limit of the inner-zone. On the lateral surface however when the cranial limit of the inner-zone begins to converge, (consequently begins to move in a caudal direction), it deviates strongly diverging (consequently in a cranial direction). The outer-zone hereby becomes rather wide; at the v. d. it attains a width of 21 mm. The caudal limit of the outer-zone follows that of the inner-zone as far as the lateral surface, then about the place where likewise the cranial limits of outer- and inner-zone deviate from each other, it takes also a diverging direction (consequently follows a caudal course). In the level of the axil-groin-fold line the outer-zone reaches its greatest width. From here it continues in a ventral direction pretty well perpendicular to the axis of the body. The caudal outer-zone is at the v. d. only 12 mm. wide.

If now we cast a glance at the entire strychnine-segmentzone, i.e. both inner- and outer-zone, we obtain the impression, that the two zones by which it is formed (both inner- and outer-zone) show an inclination to shrinking. In favour of this view plead: 1. the stronger converging of the limits of the inner-zone towards the ventral diameter, which reminds us of W. and v. R.'s central area; 2. the fact that the cranial outer-zone exceeds the caudal-zone especially in the ventral region; 3. the disappearance of a distinct "ventral crossed overlap"; 4. the fact that at the d. d. the zone is as wide as the former (VIII<sup>th</sup> Th.) and is here 34 mm., whilst at the v. d. the width is here 49 mm., consequently 6 mm. less.

If we may admit here on these grounds a first beginning of shrinking, then we are struck by the fact that the zone undergoes this diminution exactly in its most excentric part, namely in the "ventral-crossed overlap" and farther in the caudo-ventral region. In this way we obtain an insight into the manner in which the shrinking begins, and must observe then, that this shows conformity with what SHERRINGTON and W. and v. R. saw already in their root-fields.

We may consequently admit, that both the dermatomes and the strychnine-segmentzones, when they shrink, do so in the same manner, and both have their weakest point in the ventral-crossed overlap-region and in the caudo-ventral part.

### 3. *Strychnine-segmentzone of Th. VII right.*

As after the expiration of the above-mentioned determinations, the cat was still in a very good condition, I undertook the poisoning of another root, now on the right side of the spinal cord. I selected for this operation Th. VII, where I performed the application of the strychnine as carefully as possible, and did not cut the adjoining roots. I had previously convinced myself that to the right there was not a vestige of hyperreflexion in the skin. At the same time the first isolated root Th. VIII to the left was cut.

After the poisoning soon a distinctly hyperreflectory zone appeared that could easily be limited.

The zone had a great extent now, and no distinct contrasts between the inner- and the outer-zone could be discovered.

#### *Description of the total zone of Th. VII right.*

The cranial limit leaves the d. d. at about the level of the processus spinosus of the 7<sup>th</sup> thoracal vertebra, and runs almost perpendicularly to the axis of the body, with slight convexity in a caudal direction on the lateral surface. On the ventral surface it deviates again somewhat more in a cranial direction. The v. d. is reached 10 mm. cranially from the cranial limit of the left VIII<sup>th</sup> thoracal zone. (Comp. figure 3).

The caudal limit leaves the d.d. about 30 mm. caudally from the former and runs almost parallel with it with a slight inclination to diverging in a caudal direction. It reaches the v. d. together with the caudal limit of the left VIII<sup>th</sup> thoracal zone. (Compare the description given above and fig. 3). In the v. d. the width of the whole zone amounts to 43 mm. A ventral-crossed overlap could not be ascertained. This fact and likewise the comparatively slight width of the zone can justify the supposition that we have here to do with a beginning of shrinking, at all events the zone as strychnine-segmentzone has not the maximum extent which it can have. (Th. VIII on the left side was much wider). Although we have here not even to do with an optimum, I found, when exactly fixing the limits in the fixed bone-points under the skin, that the extent on the lateral surface answered already to above 3 ribs and the spaces between 3 ribs.

Such an extent is now the same as MERTENS could preparatorily ascertain as the norm for the trunk-dermatome of man.

The trapezium-shape answers likewise to the anatomical dermatome: all these proportions consequently plead strongly for the fact that my method is superior to the usual isolation methods, and strengthen the view, that the strychnine-segmentzone represents in fact the whole rootfield: the theoretical dermatome. If this is so indeed, we may likewise conclude that W. and v. R's view, that the central area and the whole dermatome have the greatest width in the lateral part, is not correct, but that the greatest width is reached at the v. d. <sup>1)</sup>.

At last we can try, by a comparison of the dimensions of the zones which we have found, to get an insight into the overlappings of the root-fields. With a view to this I begin to represent here all the dimensions found by me in a table likewise indicating those of the areflectory zone of the left side, situated between the isolated Th. VIII and Th XI.

	Width	d.d.	Lat. line	Pap. line	v. d.
Strychnine-segmentzone of Th. VIII.	inner-zone	30	30	24	23
	cranial outer-zone	2	7	10	10
	caudal outer-zone	3	13	16	21
Total width of the str.segm.zone		35	50	50	54
Areflectoric zone		11	6	10	10
Strychnine-segmentzone of Th. XI	inner-zone	32-34	28	26	16
	cranial outer-zone	?	17	15	21
	caudal outer-zone	?	10	12	12
Total width of Th. XI		34	55	53	49
Strychnine-segmentzone of Th. VII	total width of the zone	30	?	?	43

<sup>1)</sup> Compare: V. E. MERTENS. Ueber die Hautzweige der Intercostalnerve. Anatom. Anzeiger Bd. XIV. S 74 Jena. 1891. MERTENS describes here the extent i.a. of the 4th intercostalnerve of man. He found: that the zone provided for by it: . . . "sich über drei Intercostalräume, und ebensoviel Rippen erstreckte, und zwar begann es mit dem dritten Intercostalraum, und endete auf der sechsten Rippe".

As it is known W. and v. R. indicate the overlapping of the central-area as  $\frac{1}{3}$  of the extent at the d. d. Further they found, in some of their cases, that the width of the analgic zone, the consequence of the cutting of two roots, was as wide at the d.d. as the sensible zone of one isolated root.

Let us now compare the results of the strychnine-segmentzones.

With regard to the proportion of the width of one total segmentzone to that of the areflectory zone of two cut roots we see that the proportion is here 30 : 15, thus instead of 1 : 1 they bear a proportion of 2 : 1. Of greater importance however is the overlapping of the strychninezones in their entirety, or, where they have taught us to consider them, identical with the theoretical dermatomes, the overlappings of the entire rootzones. W. and v. R. could not determine them, as is self-evident, because they always found large "marginal area".

If we apply now the method of calculation of the covering as indicated by the above-mentioned authors we find, if we call the overlapped field of the root-zones  $x$  and the not overlapped part  $y$ , that at the d.d. holds for the whole hyperreflectoric zone

$$2x + y = 35 \text{ m.m.}$$

and the areflectory zone must be expressed as :

$$2y + x = 11 \text{ m.m.}$$

From this we can calculate the values of  $x$  and  $y$

$$\begin{array}{rcl} 2x + y = 35 & 2x + y = 105:3 & x + 2y = 33:3 \\ 2y + x = 11 & x + y = 46:3 & x + y = 46:3 \\ \hline 3x + 3y = 46 & x = 59:3 & y = -13:3 \end{array}$$

From which follows that

$$\begin{aligned} x : y &= 59 : -13 \\ y &= -\frac{13}{59}x = -\frac{2}{9}x. \end{aligned}$$

If now we suppose the whole root-zone = 1, then is

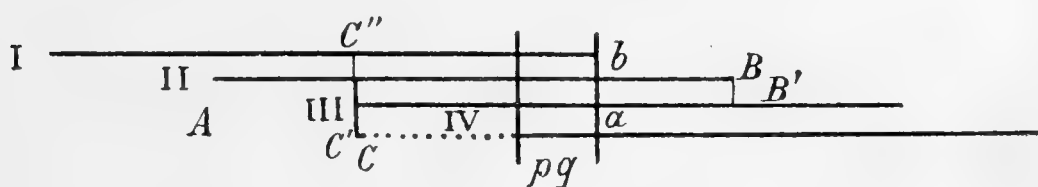
$$2x + y = 2x - \frac{2}{9}x = 1, \text{ consequently } 16x = 9, \text{ and } x = \frac{9}{16}.$$

From this follows that the rootfields cover each other at the d.d. for  $\frac{9}{16}$ . W. and v. R. had estimated it at about  $\frac{9}{15}$ , which agrees pretty well with my result.

From the construed figure (fig. 4) it appears that in the dorsal trunkskin, parts are alternately provided for by two and by three

roots. In the middle of each dermatome meet each other the outer extremities of the two adjacent zones, which overlap each other here for  $\frac{2}{16}$ . Here consequently a threefold root-innervation takes place. In the rest of the dermatome only two fields overlap each other.

Let us now execute the same calculation for the v.d. Here, as will be remembered, no areflectory zone was found. We can however make an analogous, though somewhat more complicated calculation, taking into account the ascertained overlapping of the zones of Th. VIII and Th. XI.



If we express now the width of the whole dermatome in the v.d. in the above indicated symbols, the width of a rootfield  $AB = Ab - B'C' - bC'' = 2x - y$ .

In the figure zone I represents consequently Th. VIII and zone IV Th. XI. As Th. VIII and XI overlap each other 10 m.m. I may suppose  $pq = 10$ . If now we call  $x$  the overlapping of two adjacent zones, and  $y$  the overlapping of two alternating zones, then we find for  $pq$ :

$$pq = Cq - Cp = C'a - bB \text{ as } Cp = bB$$

$$pq = y - (AB - Ab) \quad \text{as } C'a = y \text{ (namely the overlapping of I on III)}$$

$$pq = y - (2x - y - x)$$

$$pq = y - x + y = -x + 2y = 10 \text{ m.m.}$$

From this follows:

$$\begin{array}{rcl} 2x - y = 55^1) & -x + 2y = 10 & \\ -2x + 4y = 20 & 4x - 2y = 110 & \\ \hline 3y = 75 & 3x = 120 & \\ y = 25 & x = 40 & \end{array}$$

The overlapping of the immediately adjacent root-fields ( $x$ ) is consequently

<sup>1)</sup> I take here for the calculation the width of Th. VIII and not that of Th. XI, because I suppose that this zone had somewhat shrunk.

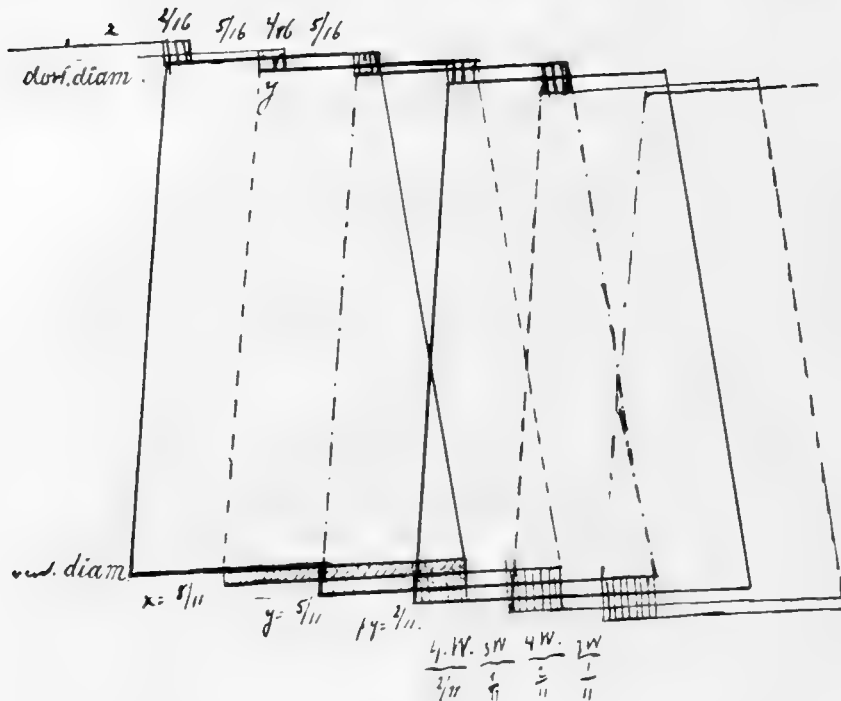


Fig. 4.

Scheme of the mutual overlappings of the dermatomes at the d.d. and at the v.d. (The dorso-ventral dimension has not been taken proportionally correct.

$\frac{40}{55} = \frac{8}{11}$ ; and the overlapping of a root-field with the third next one ( $y$ ) is  $\frac{25}{55} = \frac{5}{11}$ . At last the overlapping of a rootfield with the fourth ( $pq$ ):  $\frac{10}{55} = \frac{2}{11}$ .

W. and v. R. supposed that the rootzones overlap each other for one half, so that zone 1 should stand against zone 3. Consequently each skinpoint would be provided for by only two roots. From my statements it appears that the overlaps are much stronger, and that in some places even as many as four rootfields overlap one another. The arrangement is thus at the v.d. so, that here strips that are provided for by 2 borders of rootzones and by 2 more central parts of these, alternate with strips provided for by the more peripheral parts of three rootfields.

If we repeat the calculations given above likewise for the "inner-zones" of my strychnine-segment zones, then the overlapping of these at the d.d. appears to be not  $\frac{1}{3}$ , as W. and v. R. supposed, but  $\frac{1}{2}$ .

At the ventral median line where W. and v. R. did not find an overlap of their central areas, the overlaps of the inner-zones appears to be about  $\frac{1}{5}$ . From this great difference between the results of

I. J. H. M. KLESSENS. "From and function of the trunk-dermatome tested by the strychnine-segmentzones".



Fig. 1. Left side of 32. Inner- and outer-zones of Th. VIII. (*a d p q*) and of Th. XI. (*e f m n*). (Indicated the arcus costarum and the scapula and the crista ilei)

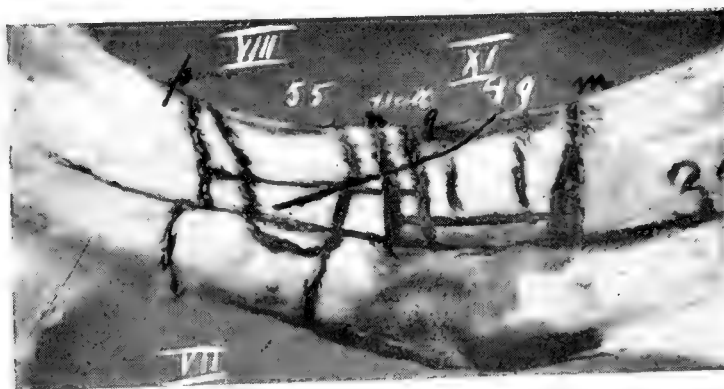


Fig. 2. Ventral side of cat 32. To the left the inner- and outer-zones of Th. VIII (*p q*) and of Th. XI (*n d*). To the right the total zone of Th. VII.



Fig. 3. Right side of cat 32. Strychnine-zone of Th. VII. (Indicated the arcus costarum and the scapula).





the usual method of isolation and mine appears again how strong a diminution of the limited value of stimuli is obtained by strychnine.

So far the facts. Now it seems not impossible to me to investigate, with the help of my results, somewhat closer some questionable points of the segmental innervation.

Let us begin with the well-known so called "LANGELAAN lines". According to this author<sup>1)</sup> one finds in the skin of normal persons hyperaesthetic lines and strings, which are said to exist in the intersegmental limits. From my calculations of the overlaps it might follow on the contrary, that there is a better foundation for admitting this hyperaesthesia in those strips of skin where always three (at the d.d.) dermatomes overlap each other. These strips however do not lie intersegmental in the sense of two immediately succeeding zones, but exactly opposite to the axis of a rootfield. At the same time they form the so-called intersegmental limit of each third dermatome: From this may, at the same time, be concluded that the distance between two "LANGELAAN lines" does not amount to the width of a dermatome, but to half the width. At the v. d. the proportions are too complicated for an analogous interpretation to be ventured.

For the much discussed territory of pigment-stripes of vertebrae the knowledge of the innervation-proportions of the skin, as it is now somewhat more detailed by the study of the strychnine-segmentzone, might prove useful. I have here specially in view the dark stripes of so many animals. SHERRINGTON<sup>2)</sup> has already called the attention to the fact that with zebra and tiger they seem to be segmentally arranged. VAN RIJNBEEK<sup>3)</sup> considers the dark stripes as an expression of the stronger innervation which in his opinion can be observed in the intersegmental limits. By the overlaps of the central area a "summation" of the innervation is supposed to exist.

It is clear that to this view may be applied likewise what I said already above with regard to the "Langelaan-lines". Then VAN RIJNBEEK's excess-contrasts might be arranged in those strips where the extreme borders of the alternating dermatomes overlap one another.

At last we may here fix the attention of the proportion in length of the short basis of the trapezium-shaped dermatome (in the d.d.) to that of the long basis in the v.d. This proportion is in Th. VIII

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1) J. LANGELAAN. On the determination of sensory spinal skinfields in healthy individuals. These Proc. of 29 Sept. 1909 Vol. III.

2) C. S. SHERRINGTON. l. c. p. 737.

3) G. VAN RIJNBEEK De huidteekeningen der gewervelde dieren in verband met de segmentaalleer. Verslagen der K. Akademie v. Wetenschappen te Amsterdam, 30 Sept. 1905.

zone here described, as 2 : 3. (In reality the proportions were 35 : 55). It is certainly peculiar, that this proportion 2 : 3 expresses exactly the "stretching" of the ventral skin (from manubrium to symphysis) with regard to the dorsal one from the first to the thirteenth thoracal vertebra. I could find for the cat about the same proportion, given by SHERRINGTON for *Macacus*.

*Summary :*

I. In favourable cases the strychnine-segmentzone has the exact shape, and most likely also entirely the same extent as the theoretical dermatome. It has then the shape of a trapezium, the short basis of which lies in the dorsal, and the long basis in the ventral body-diameter.

II. The strychnine-segmentzone consists of two parts which are sharply to be distinguished: an "inner-zone" that becomes sooner hyperreflectory, and remains stronger, and an "outer-zone" that appears later and remains less hyperreflectory. This behaviour of the strychnine-zone is consequently analogous to what SHERRINGTON and especially W. and v. R. communicated already about the sensibility in the dermatome that they had investigated by the isolation-method.

III. The vulnerability of the strychnine-segmentzone shows likewise great correspondence with that of the isolated root-field; they begin to shrink in the ventral overlapzone, and in the caudo-ventral part of the zone. Moreover they offer like the root-fields the peculiarity, that when shrinking, the innerzone analogous to the nucleusfield, becomes smaller, to the advantage of the outer-zone, analogous to the border-zone.

IV. In consequence of all this we may admit that the other proportions found for the strychnine-segmentzone, hold likewise for the dermatomes, that is to say :

the overlapping of the d.d. amounts to  $\frac{9}{16}$  and at the v.d.  $\frac{8}{11}$ . By this the skin is alternately provided for: at the d.d. for  $\frac{2}{16}$  by three roots, and for  $\frac{5}{16}$  of each dermatome by two roots; and at the v.d. for  $\frac{2}{11}$  by four roots, and for  $\frac{1}{11}$  of each dermatome by three roots.

V. The "Langelaan lines" and VAN RIJNBEEK's "excess-contrasts" by summation most likely answer to the strips of skin, where, at the dorsal diameter, the innervation takes place through three roots. If this hypothesis might be confirmed we should in the mentioned skin-stripes really possess a means of fixing the dermatome limits, as between every two such like alternating stripes, exactly a dermatome would be situated.

**Microbiology.** — “*Action of hydrogenious, boric acid, copper, manganese, zinc and rubidium on the metabolism of Aspergillus niger*”. By Mr. H. J. WATERMAN. (Communicated by Prof. M. W. BEIJERINCK).

(Communicated in the meeting of Oct. 26, 1912).

RAULIN's object when examining the culture conditions of *Aspergillus niger*<sup>1)</sup> was to obtain the greatest possible weight of mould.

The experimenters who after him occupied themselves with this question, likewise only considered the dry weight.

Such an investigation must needs be partial as the process of the metabolism is only roughly determined by the weight of mould. For a good insight into this process it must be observed that for instance the spore formation produces differences in the chemical composition of the obtained mould materials.

Hence, the changes of the plastic aequivalent or of the assimilation quotient should be determined many times in the course of the development; first of all of the carbon then of the other elements.

In an earlier paper<sup>2)</sup> I proved that changes of temperature and concentration do not modify the metabolism of the carbon and that only the velocity of this process is subject to modification.

At present I have studied the influence of various chemical compounds.

#### 1. *Action of different rates of hydrogenions.*

The results of the referring experiments are found in Table I.

We see from it in connection with the incorrectness of these observations, caused by the small quantity of mould, that the plastic aequivalent of the carbon, in spite of the slackening of the growth and sporeforming, caused by the hydrogenions, does not undergo a convincing change.

#### 2. *Action of different boric acid concentrations.*<sup>3)</sup>

Analogous results as for the hydrogenions were found with boric acid as seen in Table II.

In lower concentrations of about 0,06‰ the plastic aequivalent remains almost unchanged.

The slight lowering observed at higher concentrations may be

<sup>1)</sup> J. RAULIN, Etudes chimiques sur la végétation, Paris 1870.

<sup>2)</sup> H. J. WATERMAN, Beitrag zur Kenntnis der Kohlenstoffnahrung von *Aspergillus niger*, Folia Microbiologica, Holländische Beiträge zur gesammten Mikrobiologie 1912 Bd. I p. 422.

<sup>3)</sup> Also compare: J. BÖESEKEN and H. J. WATERMAN, Folia Microbiologica I (1912) p. 342.

TABLE I.

Culture liquid: 0,15 gr. paraoxybenzoic acid p. 50 cm<sup>3</sup> tapwater. Temp. 32—33° C. Anorganic-food: 0,05% NH<sub>4</sub>Cl, 0,05 KH<sub>2</sub>PO<sub>4</sub>, and 0,02% MgSO<sub>4</sub>.

No.	H-ions in grams p.L. given as sulf acid.	Expressed in c.m <sup>3</sup> . N. H. SO <sub>4</sub> p. 100 cm <sup>3</sup> of the culture liquid	Course of development <sup>1)</sup> after					Plastic. Aeq. of the carbon after	
			2	5	9	27,28	40	27—28	90 days
1	0	0	++	++++	++++++ many spores	as after 9 days		57%	
2	0	0	++	++++	= 1			47,,	
3	0,4 · 10 <sup>-5</sup>	0,19	++	++++	= 2	As after 9 days; the quantity of spores diminishes considerably from N <sup>o</sup> . 5 to N <sup>o</sup> . 9.		55%	
4	1,1 · 10 <sup>-5</sup>	0,58	++	++++	= 3		49,,		
5	1,8 · 10 <sup>-5</sup>	0,97	++	++++	+++++ <sup>2)</sup>		48,,		
6	2,1 · 10 <sup>-5</sup>	1,17	++	++++	++++ ++ few spores		44,,		
7	2,8 · 10 <sup>-5</sup>	1,56	+	++	+++ <sup>2)</sup> few spores		43,,		
8	3,3 · 10 <sup>-5</sup>	1,96	+	++	+++ <sup>2)</sup> few spores		46,,		
9	3,9 · 10 <sup>-5</sup>	2,35	—	+	+++ <sup>2)</sup> few spores		43,,		
10	4,4 · 10 <sup>-5</sup>	2,74	—	—	?				
11	5,7 · 10 <sup>-5</sup>	3,92	—	—	—				

TABLE II.

50 cm<sup>3</sup> tapwater, in which dissolved 1 gr. glucose, 0,15% NH<sub>4</sub>NO<sub>3</sub>, 0,15% KH<sub>2</sub>PO<sub>4</sub>, 0,06% MgSO<sub>4</sub>. Temp.: 33 - 34° C.

Nr.	Weight of boric acid added in %	Development after		Plastic aequiv. of the carbon after 7 days
		2	6	
1	0	+++	vig. growth, many spores	36 %
2	0,01	+++	" " " "	36,5,,
3	0,02	+++	" " " "	35,,
4	0,06	+++	" " " "	34,,
5	0,2	+++	" " " "	31,,
6	0,5	++	+++++, few spores	30,,
7	1,0	+	+++ , no spores	—

<sup>1)</sup> The differences in vigour of mycelial growth are indicated by "++", "++++", "+++++" etc.

<sup>2)</sup> The mycelium is yellow.

explained by the formerly described mutation <sup>1)</sup> occurring under the influence of boric acid.

From these observations it follows that the metabolism of the carbon, in opposition to the velocity of the growth and spore production, changes little by the said chemical influences.

### 3. Action of copper.

Whilst RAULIN <sup>2)</sup>, proved that coppersulfate in strong concentrations is noxious to the development of *Aspergillus niger*, RICHTER and ONO put the question whether copper in very dilute solutions may act favourably.

ANDREAS RICHTER <sup>3)</sup>, who stated that in absence of zinc even addition of  $\frac{1}{150000000}$  gr.mol. coppersulfate per L. caused the weight of mould to decrease, answers this question negatively.

N. ONO <sup>4)</sup> came to an opposite result.

The observations of ONO and RICHTER need not, however, be in contradiction with each other as it is not certain that they cultivated under the same circumstances, although ONO endeavoured to do so.

ONO's experiments especially are deficient in as much as the velocity and the nature of the metabolism are not sufficiently separated. For this reason I have once more made an analogous investigation.

The chemicals used were of KAHLBAUM'S and of great purity.

The distilled water was once more purified by redistillation in an apparatus of Jena glass joined by a glass tube to a tin cooler <sup>5)</sup>, and then kept for use in Jena flasks. The cultivation took place in ERLIENMEYER flasks of Jena glass of 200 cm<sup>3</sup>. capacity.

The composition of the culture liquid was:

0.15 %	ammoniumnitrate
0.1	„ potassium-chloride
0.1	„ magnesiumsulfate (crystallised)
0.05	„ calciumnitrate (free from water)
0.05	„ fosforic acid (crystallised)
2	„ glucose.

<sup>1)</sup> H. J. WATERMAN, These proceedings, June 1912. Vol. XV, p. 124.

<sup>2)</sup> l. c. p. 136.

<sup>3)</sup> A. RICHTER, Centralbl. f. Bakteriol. 2e Abth. Bd. 7 (1901) p. 417.

<sup>4)</sup> N. ONO. Centralbl. f. Bakteriol. 2e Abth. Bd. 9 (1902) p. 154.

<sup>5)</sup> Corks and such like material were avoided.

Each culture tube was filled with 50 cm<sup>3</sup>. of the above liquid and coppersulfate was added in different concentrations.

After boiling spores of *Aspergillus niger* (Form I) <sup>1)</sup> were inoculated.

The observed development is described in Table III; the formation of but few spores is caused by the use of the said chemicals free from manganese, as is further explained in Table V.

T A B L E III.  
Temp. 34–35° C.

Nr.	Coppersulfate added (Cu SO <sub>4</sub> . 5 Aq.)		Course of development after			
	In milligr.	In Gr. mol. p. Litre	1	3	5	9 days
1	Control	—	+	rather vigorous, hardly any spores	vigorous, hardly any spores	vigorous, only few spores
2	0,01	$\frac{8}{10\ 000\ 000}$	+	= 1	= 1	vigorous, very few spores
3	0,1	$\frac{8}{1\ 000\ 000}$	+	= 2	= 2	vigorous, hardly any spores
4	1,0	$\frac{8}{100\ 000}$	+	++	+++ , hardly any spores	++++ , hardly any spores
5	3,5	$\frac{2,8}{10\ 000}$	+	++	++ , hardly any spores	+++ , hardly any spores
6	9	$\frac{7,2}{10\ 000}$	+	++	+++ , hardly any spores	++++ , hardly any spores
7	26,5	$\frac{2,12}{1000}$	+	+ - ++	++ , hardly any spores	+++ , hardly any spores
8	52	$\frac{4,16}{1000}$	+	+	++ , few spores	++++ , hardly any spores
9	100	$\frac{8}{1000}$	+	+	++ , few spores	+++ , hardly any spores
10	252	$\frac{2}{100}$	?	—	?	+, hardly any spores
11	505,5	$\frac{4}{100}$	—	—	after two months' growth, but probably with mutation	
12	1000	$\frac{8}{100}$	—	—	—	—

<sup>1)</sup> Compare H. J. WATERMAN. These Proceedings June 1912.

We see that already  $\frac{8}{10000000}$  gr. mol. coppersulfate strongly diminishes the production of spores.

The velocity of the mycelium formation as well as the assimilation of glucose are also slackened by the coppersulfate (Comp. Nr. 4 and the following Nrs with Nrs 1--3).

By determining the quantity of dry substance <sup>1)</sup> and the carbonic acid obtained from it by combustion on one hand, and on the other, by determining the polarisation <sup>2)</sup> and the reduction number by titration after FEHLING, by which the assimilated glucose could be computed, the plastic aequivalent of the carbon could be fixed.

In Table IV the results of these experiments are united.

T A B L E IV <sup>3)</sup>.

Metabolism of *Aspergillus niger* under influence of different coppersulfate concentrations. Nine days after inoculation.

Nr.	Obtained dry weight in milligrs.	Mgr. CO <sub>2</sub> at combustion of the mould material	Assimilated glucose in %	Plastic aeq. of the carbon.
1	306	530	100	36,0%
2	318,5	556	100	38,0 "
3	325,5	563,5	100	38,5 "
4	377	643,5	100	44,0 "
5	148	257,5	52	34 "
6	190,5	331	57	39,5 "
7	83	146	31	32 "
8	112	192,5	32	41 "
9	89,5	158,5	26	41,5 "
10	6,5	—	6	—
11	—	—	0	—
12	—	—	0	—

<sup>1)</sup> Dried at 105° to constant weight.

<sup>2)</sup> Determined by the saccharimeter of SCHMIDT and HAENSCH. It is proved that in the Nrs. 1--6 a small quantity of a hitherto unknown polarising substance occurred, not reduced by "FEHLING".

<sup>3)</sup> Compare Table III.

We thus observe that the addition of  $\frac{8}{100000}$  gr. mol. coppersulfate considerably enhances the weight of mould after 9 days; it is more than 70 milligr. greater than that obtained without addition of copper.

Already before<sup>1)</sup> I explained that the non-formation of spores commonly coincides with the accumulation of glycogen in the mould and with a high plastic equivalent of the carbon.

This we find confirmed here, compare for instance Nrs. 1, 2, 3, 4.

The values of the then following numbers are not very exact. That they are notwithstanding mentioned is to make clear that even considerable copper concentrations (N<sup>o</sup>. 9) do not change the character of the metabolism. The decrease in quickness of the assimilation of glucose is very obviously caused even by slight quantities of copper.

Whether the greater mould production may be called favourable is doubtful, the sporeforming being retarded.

#### 4. *Action of manganese.*

BERTRAND and JAVILLIER<sup>2)</sup> found that addition of manganese enhances the weight of mould whilst it was also stated that this element is fixed in the organism. It also proved necessary for the spore forming<sup>3)</sup>.

By a very minute examination BERTRAND succeeded in showing that even addition of  $\frac{1}{10000000000}$  manganese made the weight of mould rise considerably. As will be seen from Table V the addition of manganese had especially brought about changes in the velocity of the glucose assimilation. For the rest, my experiments with manganese have confirmed those of BERTRAND and JAVILLIER.

The composition of the nutrient liquid was :

very pure distilled water in which dissolved:

- 0.15 % ammoniumnitrate
- 0.1 „ potassium chloride
- 0.1 „ magnesiumsulfate (crystallised)
- 0.05 „ calciumnitrate (free from water)
- 0.05 „ ammoniumfosfate
- 0.05 „ fosforic acid (crystallised)
- 2.— „ glucose

<sup>1)</sup> H. J. WATERMAN, *Folia Microbiologica* I. (1912) p. 422.

<sup>2)</sup> BERTRAND et JAVILLIER. Influence du manganèse sur le développement de l'*Aspergillus niger*. C. r. **152** (1911) p. 225; Ann. de l'Institut Pasteur T. **26** (1912) 25 Avril p. 241.

<sup>3)</sup> BERTRAND. Extraordinaire sensibilité de l'*Aspergillus niger* vis à vis du manganèse. C. r. **154** (1912) p. 616.



Into each ERLLENMEIJER flask of Jena glass (200 cm<sup>3</sup> capacity) 50 cm<sup>3</sup> of the above liquid was introduced and manganese in different concentrations was added.

For the result see Table V.

Quite as in the preceding experiment every nr. consisted of several flasks. Taking this into consideration, the extreme sensibility of *Aspergillus niger* as to manganese, already observed by BERTRAND, was with certainty confirmed. Without manganese hardly any spores are formed after four days.

In spite of the observed favourable influence of manganese on the production of spores no important modifications in the metabolism of the carbon occur (Table V).

We may thus conclude that the numbers given by BERTRAND<sup>1)</sup> for the dry weight with and without addition of manganese relate only to the velocity of the metabolism.

Is it necessary or desirable to distinguish elements such as manganese from others as carbon, nitrogen, etc. which occur in the organism in great percentages? Have we to reckon manganese among the purely catalytic elements, in opposition to carbon as a plastic one? In my opinion there is no sufficient reason for such a marked separation. The only important difference is that elements as manganese form an extremely small permanent percentage of the organism. It is, however, very well possible that this difference is only apparent. The circulation of manganese may for instance be much quicker than that of carbon, so that the concentration in one special cell may for a time have been relatively high. It is not, however, possible to detect this by analysis of the whole mould layer.

### 5. Action of zinc.

Since RAULIN had already supposed that zinc acts favourably on the weight of mould, JAVILLIER<sup>2)</sup> showed with certainty that small quantities of zinc considerably increase this weight. At the same time he proved that zinc is fixed in the mycelium<sup>3)</sup>. Moreover, BERTRAND and JAVILLIER<sup>4)</sup> studied the joint action of zinc and man-

<sup>1)</sup> BERTRAND C. r. **154** (1912) p. 616.

<sup>2)</sup> JAVILLIER, Sur l'influence favorable de petites doses de zinc sur la végétation de *l'Aspergillus niger*, C.r. **145** (1907) p. 1212.

Also compare BERTRAND et JAVILLIER, Sur une methode permettant de doser de très petites quantités de zinc C. r. **143** (1906) p. 900; **145** (1907) p. 924.

<sup>3)</sup> Sur la fixation du zinc par *l'Aspergillus niger*. C. r. **146** (1908) p. 365.

<sup>4)</sup> BERTRAND et JAVILLIER, C. r. **152** (1911) p. 900; C. r. **153** (1911) p. 1337. Cf. also Ann. de l'Inst. Pasteur T. XXVI (25 Juillet 1912) p. 515.

ganese, which proved more favourable than that of each of these elements separately.

In his last communication JAVILLIER<sup>1)</sup> mentioned that the constant relation between the assimilation of sugar and the production of mould, which is nearly 3 : 1, sometimes became 8 : 1 by leaving out zinc, that is to say, addition of zinc should allow the organism to use less food; besides, the assimilation of nitrogen and of the other anorganic elements changed according as zinc was added or not.

Hitherto I have not been able to confirm JAVILLIER's results. Addition of zinc caused but little change in the metabolism of the carbon, but again the velocity of the glucose assimilation was modified.

Addition of stronger zinc concentration:  $\frac{75}{100000}$  gr. mol.  $ZnCl_2$  p. L. caused a distinct, albeit slight increase of the plastic equivalent of the carbon, but it was accompanied by non-formation of spores.

In many respects, thus, the action of zinc resembles that of copper. As with this element the addition of slight quantities of zinc, which exerts no perceptible influence on the production of spores, causes hardly any change in the weight of mould.

So, nutrient solutions containing  $\frac{7}{100.000.000}$ ,  $\frac{7}{10.000.000}$  and  $\frac{7}{1.000.000}$  gr. mol.  $ZnSO_4$  7 Aq. p. L. produced after four days respectively 407, 410 and 417 milligrs. of dry material, whilst analogous experiments, without addition of zinc, produced 406 and 408 milligrs.

The fact that stronger concentrations of zinc check the forming of spores (see above) which had also been observed by SAUTON<sup>2)</sup> and JAVILLIER<sup>3)</sup>, BERTRAND<sup>4)</sup> tries to explain by the relation existing between the quantity of manganese present on one side, and the produced mould on the other.

Thus BERTRAND says: "Lorsque au milieu nutritif on n'ajoute ni fer, ni zinc, ou seulement du fer ou du zinc, les mycéliums qui prennent naissance sont si réduits que le rapport du manganèse, introduit volontairement ou non, au poids de matière organique formée, peut

1) JAVILLIER, Influence du zinc sur la consommation par *l'Aspergillus niger*. de ses aliments hydrocarbonés, azotés et minéraux, C. r. 155 (1912) p. 190.

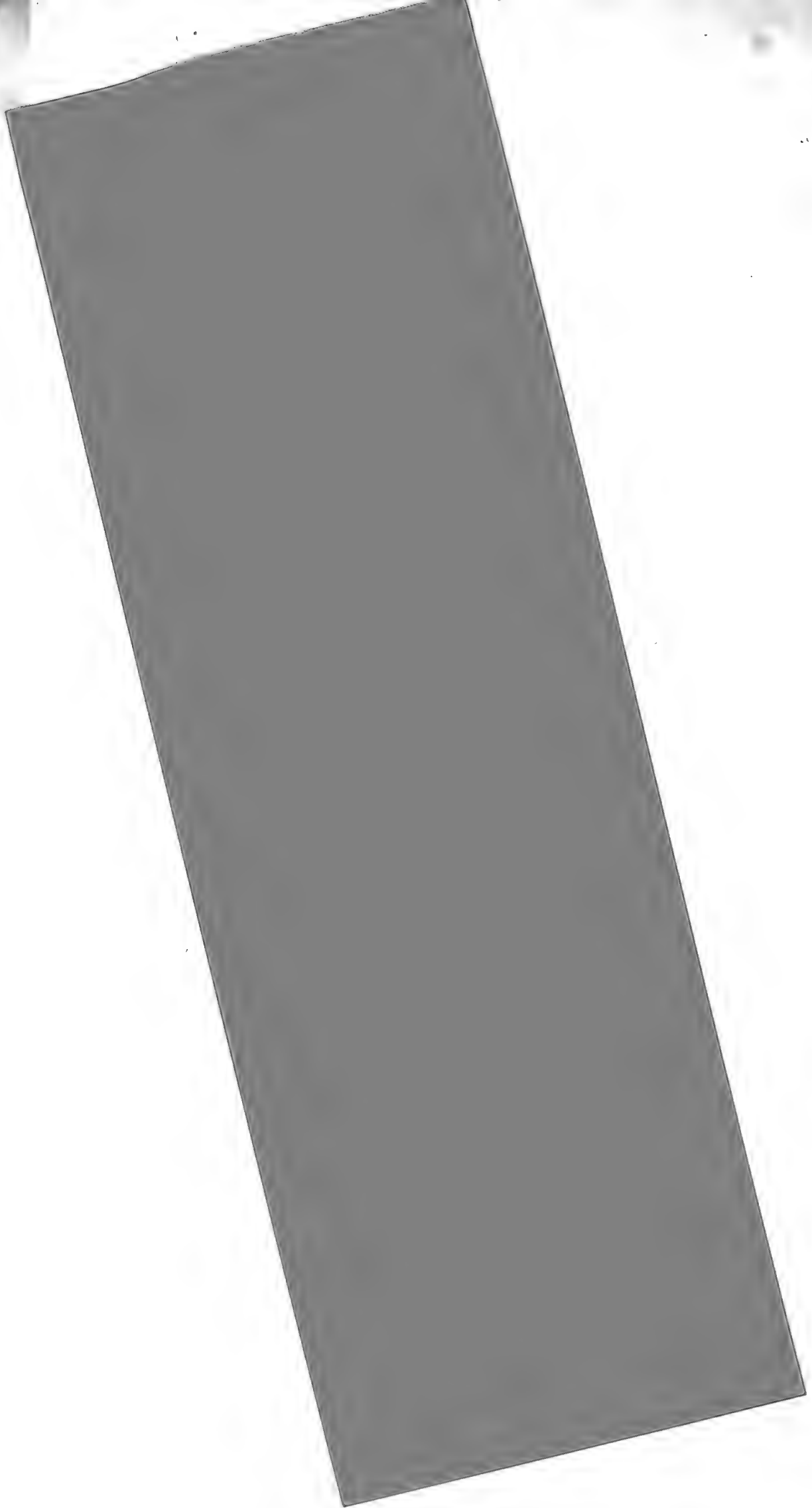
2) B. SAUTON, C. r. 151 (1911) p. 241.

3) M. JAVILLIER et B. SAUTON, Cr. 153 (1911) p. 1177.

4) G. BERTRAND, C. r. 154 (1912) p. 381.

er.

O <sub>2</sub> at end after	Assimilated glucose in pCt. after		Plastic Equivalent of the carbon after 35 days
	4	35 days	
	nearly 100 pCt.		30 pCt.
ned	undetermined		
	100 pCt.		
	"		
	nearly 100 pCt.		
	undetermined	100 pCt.	32,5
	"		33
	"		33
ned	"		
	"		35
	"		
	"		
	"		



être suffisant à la formation des conidies." On the contrary the greater the proportion of the quantity of mould material with respect to the manganese present, the smaller the production of spores.

This explanation is not, however, in accordance with my observations as the produced quantity of mould was only very little increased by the addition of zinc.

But like BERTRAND I have observed that by adding manganese, in spite of the presence of zinc, the production of spores is furthered.

Notwithstanding BERTRAND's excellent investigation only few of the factors are known which determine the formation of spores.

It is proved, however, that in the hitherto treated cases slackening of the spore formation is combined with a great plastic equivalent of the carbon.

#### 6. *Substitution of rubidium to potassium.*

In 1879 NÄGELI<sup>1)</sup> made some experiments with rubidium and caesium<sup>2)</sup> on the metabolism of *Aspergillus niger* from which he concluded that these elements could replace potassium.

BENECKE<sup>3)</sup>, who studied this question more in detail, proved that by replacing potassium by rubidium the production of mycelium was normal, but that sporeformation was inhibited.

He found that the dry weights of the rubidium moulds at the lower Rb.concentrations were somewhat higher, in other cases again lower than those obtained in a medium containing potassium. In stronger concentrations rubidium retarded the growth and only insignificant coats of mould appeared which did produce spores, which fact BENECKE could not account for. Probably the presence of potassium, if large quantities of rubidium salt are used, then becomes of importance in relation to the small weight of mycelium.

The results obtained by NÄGELI and BENECKE are here chiefly confirmed as appears from what follows.

If instead of potassiumchloride rubidiumchlorid is used the formation of mycelium remains the same. The "rubidium moulds", however, are distinguished from those cultivated with potassium by their being

<sup>1)</sup> C. v. NÄGELI, Sitzungsberichte d. math. phys. Classe d. k. b. Akad. d. Wiss. zu München vom 5 Juli 1879.

<sup>2)</sup> I have proved that caesium cannot replace potassium.

<sup>3)</sup> W. BENECKE, Ein Beitrag zur mineralischen Nahrung der Pflanzen, Ber. d. deutschen botan. Gesellschaft 1894 S. 105.

Die zur Ernährung der Schimmelpilze notwendigen Metalle, Jahrbücher für wissenschaftliche Botanik Bd. 28 (1895) S. 487.

covered with only a small quantity of spores; the rubidium mycelium is moreover more intensely yellow than in normal cases, when it often is nearly colourless.

The presence of rubidium in the said concentrations when kalium (0,1% KCl) is present has no influence on the spore formation and on the yellow-colouring of the mycelium. (See Table VI). Here it may be added that also the addition of 0.05 % manganesechloride accelerates the spore production.

For the experiment I prepared two culture media of the following composition.

Medium A:	Medium B:
Distilled water in which dissolved	Composed like A.; only instead
0.2 % ammoniumfosfate	of 0.1 % KCl, 0.1 % RbCl was
0.1 „ potassiumchloride	added.
0.07 „ magnesiumsulfate	
0.035 „ calciumchloride	
2 „ glucose	
Some drops of a dilute fosforic acid solution.	

In the careful investigation of BENECKE there is wanting an exposition of the relation between the assimilated food and the weight of mould in connection with time.

The results of more exact experiments are united in Table VII.

T A B L E VI.

Temp. 33° C.

50 cm<sup>3</sup>. of the above solutions were introduced into 200 cm<sup>3</sup>. Erlenmeyer-flasks of Jenaglas and after boiling inoculated with *Aspergillus niger*.

Nr.	Composition of the culture liquid	Growth and spore forming after		
		2	4	9 days
1 <sup>1)</sup>	50 cm <sup>3</sup> of A	++++, hardly any spores	very vigorous rather many spores	very vigorous, many spores, mycelium light yellow
2	50 cm <sup>3</sup> of A + 0,1% KCl	idem	idem	idem
3 <sup>2)</sup>	50 cm <sup>3</sup> of B	idem	very vigorous, very few spores	very vigorous, beginning of spore form. mycel. orange-col. <sup>3)</sup>

<sup>1)</sup> In triplo

<sup>2)</sup> In duplo.

<sup>3)</sup> The beginning of spore formation (Nr. 3) is probably caused by the presence of but slight quantities of potassium.

T A B L E VII.

Temp. 34—35° C.

Very pure distilled water in which dissolved: 0,15% ammoniumnitrate, 0,05% fosforic acid (crystallised), 0,1% magnesium-sulfate (crystallised), 0,1% calciumnitrate (free from water), 2% glucose (free from water). 50 cm<sup>3</sup> of the above solution was introduced into carefully cleaned ERLÉNMEIJER flasks of Jena glass, then added either 0,1% KCl, or 0,1% RbCl.

Nr.	Added	Growth and spore formation						Obtained dry weight		Mgr. CO <sub>2</sub> at combustion of the mould material	Plastic Aeq. of the carbon	
		after 1	2	3	4	6 <sup>1)</sup>	18 <sup>1)</sup> days	after 6	18		6	18
1	0,1% KCl	+	++++ not yet spores	rather vigo- rous, hardly any spores	vigorous, hardly any spores	vigorous, beginning spores form.	356	594	40,5%			
2	0,1 " KCl	+	++++ not yet spores	rather vigo- rous, hardly any spores	vigorous, hardly any spores	vigorous, beginning spores form.	217	374	41,5%	25,5%		
3	0,1 " RbCl	+	++++ not yet spores	rather vigo- rous, hardly any spores, mycelium yellow	vigorous, hardly any spores, mycelium yellow	as after 4 days	377	609,5	41,5%			
4	0,1 " RbCl	+	++++ not yet spores	rather vigo- rous, hardly any spores, mycelium yellow	vigorous, hardly any spores, myce- lium yellow	as after 4 days	268	424	29%			

<sup>1)</sup> All the glucose has disappeared from the solution.

From these it follows that the nature of the metabolism of the carbon does not change by substituting rubidium to potassium. The rubidium mycelium only proves to contain more glycogen as is shown by the greater plastic aequivalent of the carbon.

We likewise perceive that also without production of spores the digestion of the intermediary products is possible, for in spite of the fact that after 18 days at the rubidium experiment only few spores appear, the plastic aequivalent of the carbon is lowered from 41.5 to 29%,

### *Summary.*

1. Addition of 2.35 cm<sup>3</sup> normal sulfuric acid per 100 cm<sup>3</sup> culture liquid and of 0.5 % boric acid but feebly influences the plastic aequivalent of the carbon. In the case of the boric acid we must ascribe the observed changes to mutation.

2. The action of the factors that govern the development of *Aspergillus niger* must not be partially judged; thus, a high weight of mycelium cannot always be called favourable. This is not sufficiently taken into consideration by ONO, RICHTER, BERTRAND and JAVILLIER. So it was proved for the action of certain concentrations of copper sulfate, zinc chloride and zinc sulfate, that these salts considerably increase the plastic aequivalent of the carbon, whereas the increase of the weight of mould is proportional to the retarded spore production.

Very dilute zinc solutions  $\left( \frac{7}{100000000} - \frac{7}{1000000} \text{ gr. mol. ZnSO}_4 \right.$   
 7 Aq p. L.) have no influence. Coppersalts counteract the spore forming in all concentrations.

3. Presence of manganese in minimal quantities does not change the plastic aequivalent of the carbon; it only acts on the velocity of the metabolism.

The quantities of dry substance found by BERTRAND should be considered as values indicating the velocity of the process.

4. By replacing potassium by rubidium the spore formation is counteracted, the weight of mould is increased, and the metabolism of the carbon (i. e. the change of the plastic aequivalent and of the respiration aequivalent in connection with time) remains unchanged.

Finally my hearty thanks to Professor Dr. M. W. BEIJERINCK and Professor Dr. J. BÖESEKEN for their assistance in this investigation.

*Laboratories for Organic Chemistry and  
Microbiology of the Technical University.*

Delft, October 1912.



**Pathology.** — “*On a micro-organism grown in two cases of uncomplicated Malignant Granuloma.*” By ERNESTINE DE NEGRI and C. W. G. MIEREMET. (Communicated by Prof. C. H. H. SPRONCK).

(Communicated in the meeting of September 28, 1912).

In recent years Malignant Granuloma, also called Lymphomatosis granulomatosa or HODGKIN'S disease, has occupied the attention of many writers and researchers, in consequence of which some more light has been thrown upon the subject after a long period of obscurity.

For all this, the etiological evidence brought forward in the study of this incurable disease is still extremely limited.

In 1832, it is true, HODGKIN<sup>1)</sup> published the history of some cases and autopsies which may, to a certain extent, bear on the disease we are about to discuss, but its etiology was not dwelt on in the literature before many years later.

No attempt whatever had been made to distinguish by differential diagnosis the various diseases, characterised by glandular swellings and enlargement of the spleen, until VIRCHOW, in 1845, described leukaemia as a well defined disease. Next, in 1865, COHNHEIM distinguished pseudoleukaemia as a disease of the lymphatic apparatus resembling leukaemia, but differing from it by the absence of the typical bloodpicture. Since COHNHEIM the term pseudoleukaemia has again and again been misapplied to a congeries of glandular diseases; others again added the epithet “tubercular” to it, so that in spite of COHNHEIM'S discovery, the confusion was again as great as before.

Neither did BILLROTH<sup>2)</sup> confine the term “malignant lymphoma”, a name often given to malignant granuloma, to one special affection of the glands, as he himself says in his paper on Multiple Lymphome.

STERNBERG<sup>3)</sup> was the first to describe in an elaborate histological investigation a definite group of cases, thereby leading the way for later workers. He was likewise the first to discuss at length the etiology of the disease, as appears distinctly from the title of his publication: “Ueber eine eigenartige unter dem Bilde der Pseudoleukämie verlaufende Tuberkulose des Lymphatischen Apparates.” However the etiology, suggested by the title, is not nearly ascer-

<sup>1)</sup> 1832 HODGKIN. On some morbid appearances of the absorbent glands and spleen. (Med. chir. Transact. Vol 17).

<sup>2)</sup> 1871 BILLROTH. Multiple Lymphome. Erfolgreiche Behandlung mit Arsenik. (Wien. Med. Woch. N<sup>o</sup>. 44 S. 1065).

<sup>3)</sup> 1898 STERNBERG. Ueber eine eigenartige unter dem Bilde der Pseudoleukämie verlaufende Tuberkulose des Lymphatischen Apparates. (Zeitschr. f. Heilk. Bd XIX S. 21).

tained in this writing, though we must admit, that the nature of the available cases were adapted to tempt the writer to draw his conclusions. For in the great majority of cases, reported by STERNBERG, there was tuberculosis, besides the special granulation tissue described by him. As moreover in most cases tubercle bacilli were found in the histological preparations and only seldom cocci, which had caused no local reaction, so that he supposes them to have multiplied post mortem, he concludes: "dasz es eine eigenartig verlaufende Form der Tuberkulose des lymphatischen Apparates gibt".

The fact that there appears the peculiar granulation tissue, as described by him, and not a pure tubercular tissue, STERNBERG believes to be probably due to higher or lower resistibility of the patient or to the virulence of the tubercle bacillus.

At the "Siebente Tagung der Deutschen Pathologischen Gesellschaft", held in 1904, where this subject was discussed, BENDA<sup>1)</sup> advanced the theory that here we have to do with "ein sich den malignen Neubildungen näherndes Granulom welches nicht durch einen spezifischen Infektionsträger, sondern durch die modifizierten oder abgeschwächten Toxine verschiedener Infektionsträger hervorgerufen wird". ASKANAZY believes the etiology to be wholly unknown. CHIARI and YAMASAKI consider the process as a chronic inflammation whose etiology has not been ascertained, but should not be mistaken for tuberculosis. ASCHOFF arrives at the conclusion, "dasz es sich nicht um die gewöhnliche Form der Tuberkulose handelt", appealing to his failure in producing tuberculosis in 5 typical cases by inoculation of caviae. Also STERNBERG qualifies his assertions when he writes: "Wenn auch die seither publizierten Fälle diese (his) Auffassung meist bestätigten, so räume ich doch gerne ein, dasz die damals von uns gewählte Bezeichnung "eigenartige Tuberkulose des lymphatischen Apparates" vielleicht zu weit geht. Immerhin glaube ich, dasz ein Zusammenhang zwischen dem diesen Fällen zu Grunde liegenden Entzündungsprozess und der Tuberkulose nicht von der Hand zu weisen ist".

A most valuable addition to our knowledge of malignant granuloma was furnished by E. FRAENKEL and H. MUCH's<sup>2) 3)</sup> discovery of "granuläre Stäbchen", which they found to be antiformin-resistant and GRAM-positive. This at first seemed in a high degree confirmatory

1) 1904 BENDA. Zur Histologie der pseudoleukaemischen Geschwülste. (Verhandl. der D. Path. Ges. 7e Tagung 26—28 Mai).

2) 1910 E. FRAENKEL u. H. MUCH. Bemerkungen zur Aetiologie der Hodgkinschen Krankheit und der Leukaemia lymphatica. (Münch. Med. Woch. n<sup>o</sup>. 19).

3) 1910 id. id. Ueber die Hodgkinsche Krankheit (Lymphomatosis Granulomatosa) insbesondere deren Aetiologie. (Zeitschr. f. Hyg. u. Infekt. Kr. Bd. 67).

of STERNBERG's conception, considering that morphologically the granular "rods" could not be distinguished from the non-acidfast MUCH-form of tubercle bacilli. Experimental inoculation of *caviae* afforded conclusive evidence against STERNBERG's opinion. *Caviae* injected with granulation tissue obtained from uncomplicated cases were not affected by tuberculosis.

FRAENKEL and MUCH do not hesitate to call their granular rods the causative agent of malignant granuloma; however they are not decided about the question of their affinity with tuberculosis: "Die Lymphomatosis granulomatosa ist eine Infektionskrankheit, die durch granuläre Stäbchen hervorgerufen wird. Diese granuläre Stäbchen sind antiforminfest aber nicht säurefest; sie sind durch verschärfte GRAMfärbung darstellbar, und stehn dem Tuberkulose-virus zum mindesten sehr nahe. Die Lymphomatosis granulomatosa ist nach unseren Erfahrungen nur ausnahmsweise mit typischer Tuberkulose vergesellschaftet."

At a meeting held at Hamburg January 1912 FRAENKEL <sup>1)</sup> announced his discovery of "granula" or "granular rods" in 16 out of 17 cases. Availing himself of the additional evidence brought forward by MEYER, DE JOSSELIN DE JONG <sup>2)</sup> <sup>3)</sup> (who decidedly inclines to deny the identity of the tubercle bacillus with the virus of malignant granuloma both on the basis of his own experimentation and on the inoculation experiments of many other researchers), SIMMONDS and JAKOBSTHAL, FRAENKEL writes as follows:

"Es liegen jetzt über mehr als dreiszig Fälle Hodgkinscher Krankheit von den verschiedensten Beobachtern herrührende mit den unsern völlig übereinstimmende Aufgaben vor. Immerhin, das will ich offen bekennen, ist auch durch unsere Untersuchungen eine völlige Klärung der Aetiologie der Hodgkinschen Krankheit noch keineswegs herbeigeführt." And further on: "Es musz die nächste Aufgabe sein Reinkulturen der fraglichen Gebilde zu erzielen, und im Tierversuch weiter zu kommen".

It is evident that these researches did not throw more light upon the relation of the rods to the tubercle bacillus, as FRAENKEL <sup>4)</sup> him-

<sup>1)</sup> 1912 E. FRAENKEL: Ueber die sogenannte Hodgkinsche Krankheit (Lymphomatosis granulomatosa). (Deutsche med. Woch. n<sup>o</sup>. 14 S. 637).

<sup>2)</sup> 1909 R. DE JOSSELIN DE JONG. Bijdrage tot de kennis der pseudoleukaemie. (Geneesk. Bl. 14e reeks I en II).

<sup>3)</sup> 1911 id. Over acut maligne granuloom (Lymphomatosis granulomatosa). (Ned. Tijdschr. v. Gen. II helft n<sup>o</sup>. 22).

<sup>4)</sup> 1912 E. FRAENKEL u. STERNBERG. Ueber die sogenannte Pseudoleukaemie. Bericht über die XVe Tagung der Deutschen Path. Ges. in Straszburg vom 15-17 April. (Centralbl. f. Alg. P. u. Path. An. Bd. 23, No. 10).

self declares in the meeting of the Deutsche Pathologische Gesellschaft in April 1912: "Die Frage der Stellung der Granula zu den Tuberkelbazillen ist noch offen; aetiologisch ist die Lymphogranulomatose unklar."

The death of a boy v. D. S., 7 years of age, suffering from malignant granuloma, clinically uncomplicated with tuberculosis, whose autopsy took place on the 4<sup>th</sup> of June 1912, 8<sup>h</sup> 30<sup>m</sup> post mortem gave us an opportunity to cultivate the "rods", so often alluded to above. At the autopsy no trace whatever of tuberculosis was detected, only alterations pointing to malignant granuloma. The histologic examination of the spleen, a great number of glands, the bone marrow and the liver, led to the discovery of the granulation tissue which, according to STERNBERG, characterises the disease, whereas the typical alterations due to tuberculosis were not found. Nor were caviae, injected with an emulsion of the granulation tissue attacked by tuberculosis.

In smears of the spleen we could demonstrate numerous rods fully corresponding with FRAENKEL and MUCH's description of the granular rods that are found in the typical granulation tissue of the majority of such cases as were studied for this purpose. No other micro-organisms could be detected in any of the preparations.

We have been successful in demonstrating the bacteria in only a few histologic preparations, as was the case with other workers on the subject. Whether or not this was due to the small number of organisms present, we are unable to say.

In order to obtain the wished-for result, we have sown from the spleen on a large number of varying media and we have been fortunate enough to grow at once, in all the media used, a pure culture of a micro-organism, which proved in every respect similar to FRAENKEL and MUCH's rod.

It was especially on the blood-glycerine-potato-agar plate, used by BORDET to cultivate the whooping-cough bacillus, that we obtained already after 2 × 24 hrs a strongly developed culture, which proved to consist of rods morphologically in no way differing from the granular rods.

Before entering upon a description of our micro-organism we point out the fact, that we succeeded in obtaining from a jugular gland (patient S, twenty years old), sent to us for diagnosis, a micro-organism similar to that obtained post mortem from the spleen of v. D. S. The histologic examination of this gland made us decide upon malignant granuloma in making the diagnosis of the typical tissue. Tubercular changes could not be detected in the preparations, neither

were they in any way suggested clinically. PIRQUET was negative.

*Description of the Micro-organism.*

*Morphology.*

We observed the following forms varying according to the media and the age of the cultures:

**Plump short rods:** length  $1 \mu$ , breadth  $\frac{3}{4} \mu$ . The shortness of some reminds us of coccobacilli of less than  $1 \mu$  diameter (a minority on LOEFFLER'S serum; in eight-week-old cultures on Bordet medium almost exclusively; a majority on agar-plates a few days old).

**Small fine rods:** polar staining, length from  $1\frac{1}{2}$ — $2 \mu$ , breadth  $\pm \frac{3}{4} \mu$  (in every medium of any age).

**Rods of from 2—3  $\mu$  with polar granules, or more granules** (they are far predominant in the older cultures on LOEFFLER'S serum).

**Comma-shaped rods:** in many cases to be divided into two shorter rods, length  $\pm 1\frac{3}{4} \mu$ , breadth  $\frac{1}{2} \mu$  (on Bordet medium, ascites-agar, and LOEFFLER'S serum; in the first ascites-agar-culture longer and finer than in the later).

**Granular rods of different dimensions;** length varying from 5—7  $\mu$ , breadth from  $\frac{3}{4}$ — $1\frac{1}{2} \mu$ . This considerable breadth concurs with a prickly shape found on the Bordet-medium, the rods being broader in the middle and becoming more pointed towards the extremities. The greater breadth is in many bacilli due to the irregular arrangement of the protuberant granules.

In older cultures some giant forms, which however have not at all lost their original structure, i.e. a distinct body, in which the granules are seen.

Occasionally branching forms were observed in various media (Bordet-medium, fluid and solid, LOEFFLER'S serum, and canesugar-nutrose).

**Rows of granules:** only granules arranged as in the granular rods but without a visible cell-body. The arrangement is not regular, the granules being placed longitudinally in different directions relative to the long axis of the granular rod or row.

**Involution-forms:** clubbed or swollen ends (in old cultures) and spheric forms to  $2 \mu$ .

*Motility* is lacking

*Staining peculiarities:* The microbe stains easily with the ordinary dyes for bacteria. After GRAM the small rods show polar coloration, positive or negative, according to the medium; the comma-shape always positive, the body of the granular rods negative, the granules positive.

After MUCH's modification of GRAM's methods the results agree with those obtained with the Gram-stain.

With ZIEHL's stain they are not acid-fast.

*The microbe is facultative anaërobe*, however it grows much better in presence of oxygen. Growth is sluggish in deep stab-cultures, covered with agar, and in a hydrogen-atmosphere.

*Influence of temperature on the growth.*

The growth optimum is in the neighbourhood of 32° C.

The highest temperature at which growth is demonstrable is 39° C.; at 40° C. it ceases altogether.

The lowest possible temperature for growth is between 10° and 8° C. At 5° C. it is non-existent.

*Reaction of media:* alkaline reaction is more conducive to growth, which however is not inconsiderable with acid reaction.

### *Growth.*

**G e l a t i n - s t a b c u l t u r e:** not liqueficient, slight growth in the track made by the needle, threadlike, getting thinner lower down.

**S m e a r - c u l t u r e:** growing evenly in moderate amount.

**P l a t e - c u l t u r e** (after 24 hours): cultures elevated on the surface, dark grey (later greyish-yellow to ochraceous), round, smooth-rimmed, homogeneous, dewdrop-shaped, dim-glistening. Later on the colonies are finely granular and the edge gets finely crenated.

**A g a r - s t a b c u l t u r e:** slight growth in the track, threadlike, ragged, getting thinner lower down.

**S m e a r - c u l t u r e:** growing evenly in fair amount.

**P l a t e - c u l t u r e** (after 24 hours): cultures elevated on the surface, yellowish, round, smooth-rimmed, somewhat granulous, granules finer near the rim than in the centre, where a dark stain is visible, dewdrop-shape, highly glistening, condensation water cloudy, no pellicle is formed.

**A s c i t e s - a g a r - p l a t e c u l t u r e:** sluggish and slight growth; colonies finely granular, later here and there more coarsely granular especially at the periphery, so that the rim, being smooth at first, now becomes finely lobulated; elevated above the surface; fluorescence.

Young colonies dewdrop-shaped; highly glistening, condensation water as in agar-cultures.

**Broth-culture:** slow growth, cloudy with sediment, which squirms up like a slimy flagellum when shaken, and may be equally distributed. No pellicle is formed, as is the case in broth mixed with horse-serum, yeast-decoctum or ascites-fluid.

**LOEFFLER'S serum-smear-culture,** growing abundantly in 24 hours, even, very slimy.

**Plate-culture (24 hours):** highly elevated above the surface; colour deep canary-yellow, later in part brownish-red, round, smooth-rimmed, uniformly finely granular, dewdrop-shaped, moist-glistening, condensation water very cloudy; no pellicle.

Milk is not coagulated; ultimately a pinkish coloration.

**Glycerin-potato-culture:** growing badly; hardly visible, light yellow; dim-glistening.

**Blood-glycerin-potato-agar (Bordet medium):**

**Smear-culture:** abundant growth in 24 hours; the culture first obtained was greenish, afterwards rather brown to brownish-black, chocolatelike, elevated above the surface; very slimy; easy confluence of colonies; glistening; condensation water cloudy.

*Sporeformation* not noted.

*Resistance* to:

**Desiccation:** cultures in fluid media did not lose vitality at room-temperature 11 weeks after drying.

**Heating** for half an hour at 60° C. kills off the culture; when heated for 5 minutes at 80° C. they are also destroyed.

**Cold:** cultures exposed for 4 hours to a temperature of —60° C. did not lose vitality.

**Light:** diffuse daylight does not kill the microbe; nor does it affect growth.

*Lifetime:* After 16 weeks the cultures have not yet died away.

*Chemical conversions.*

**Formation of Gas:** none in broth with glucose or lactose, neither in nutrose with canesugar.

**Acid-production:** in nutrose with glycolose, mannite, maltose or canesugar.

**Alkali** has been detected in broth with yeast-decoct. After 5 weeks 1 ccm.  $\frac{5}{10}$  n. acetic acid on 9 c.c. of broth with yeast-decoct. appears to be just neutralised.

H<sub>2</sub>S is not produced.

No more is Indol.

Nitrates are not reduced to Nitrites.

Diastatic fermentation is absent.

*Chromogenesis:*

Canary-yellow mainly on LOEFFLER'S serum; less intense on the other solid media (except Bordet-medium); also in the fluid media.

Muddy green: the first cultures on Bordet-medium.

Chocolate colour on Bordet-medium.

Faint fluorescence on ascites-agar.

Brownish-red in all older cultures except ascites-agar.

*Poisonous products* could not be demonstrated.

Thus far the microbe did not prove to be pathogenic for animals, but even now we wish to lay stress on the fact that all our laboratory-animals, among which a large number of caviae, some injected with organic emulsion, others with cultures, remained free from tuberculosis.

*Summary.*

The bacterium we have been describing, is to be classed as a corynebacterium on account of:

its septed structure,

its sometimes peculiar shape with pointed or clublike extremities,

its tendency to branching,

its lack of acid-resistance (after ZIEHL) but great affinity for other bacterium stains.

We feel assured that this corynebacterium is identic with FRAENKEL and MUCH'S rods, observed by them and others in the tissue of malignant granuloma in a large number of cases.

In describing them FRAENKEL and MUCH mention their peculiar morphology, their affinity for stains, and the antiformin-resistance.

The morphological description of their rods agrees entirely with the morphology of our bacterium, as regards both the smears from the spleen and those from the cultures.

The ZIEHL- and the GRAM-stain are the same for either bacterium.

As to antiformin-resistance we discovered that it cannot be considered as a quality peculiar to this bacterium, though we too found some rods in antiformin-sediments of organic emulsion.

We do not intend to enter into further details in this short space. Further investigation will have to decide whether or not our coryne-





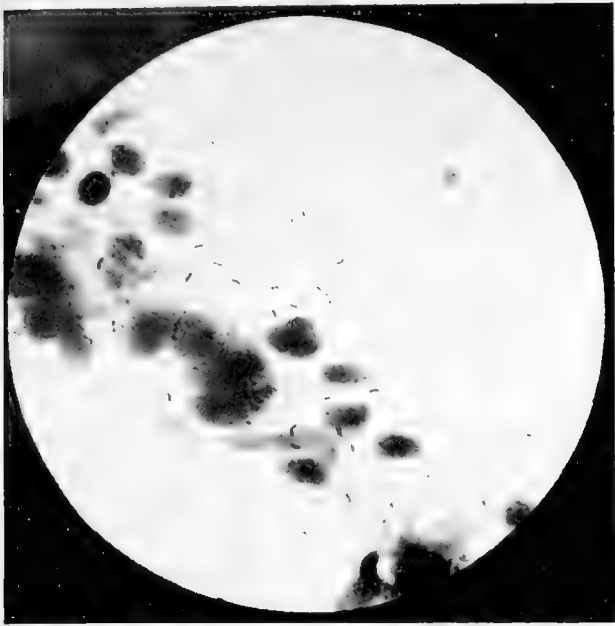


Fig. 1.

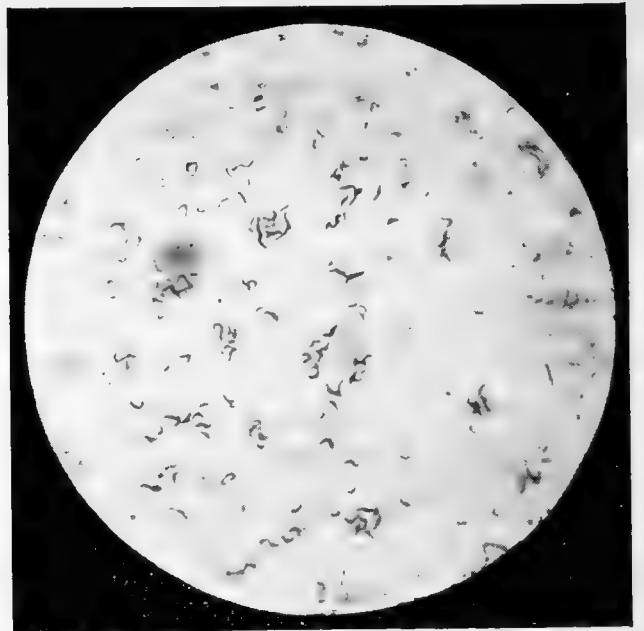


Fig. 2.

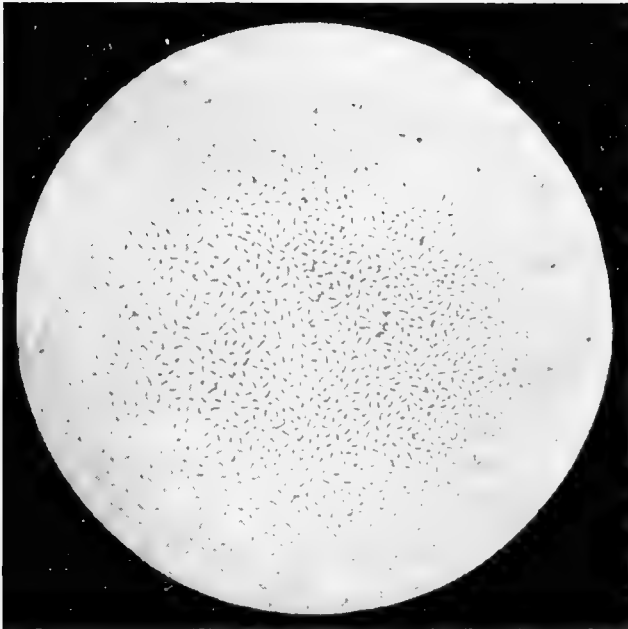


Fig. 3.



Fig. 4.

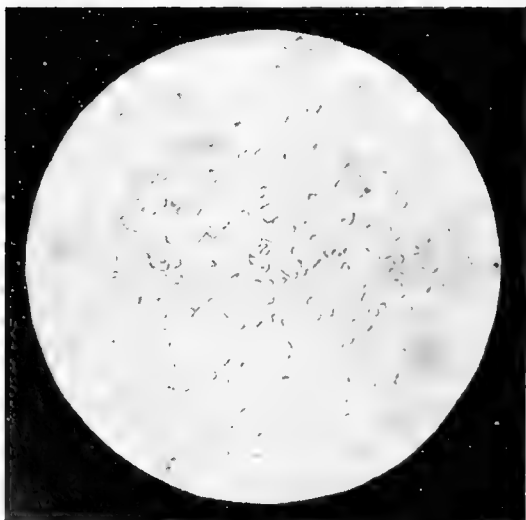


Fig. 5.

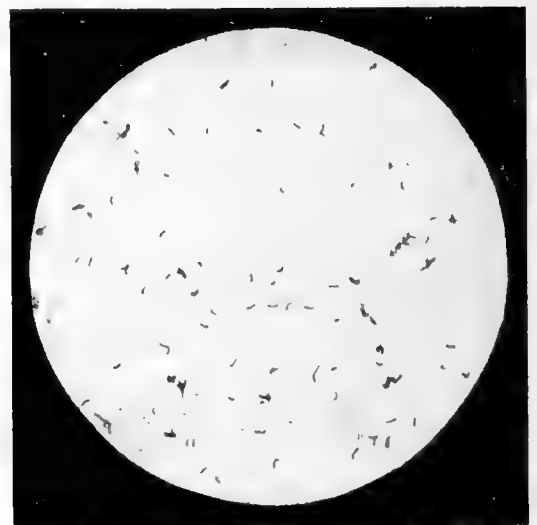


Fig. 6.

bacterium occurs invariably in malignant granuloma. In our opinion this seems to be the case, as may be concluded from the literature that appeared hitherto. Still, even if this be so, it would perhaps not by itself entitle us to consider that corynebacterium, beyond a shade of doubt, as the etiologic moment.

We purpose before long to write more at length about this subject in another publication.

#### EXPLANATION OF THE PLATE.

- Fig. I Smear from the spleen v. d. S. Gram-stain with counterstain.  
 „ II 48 hours' Bordet-culture, cultivated directly from the spleen of v. d. S. Gram-stain with counterstain.  
 „ III 18 hours' Bordet-culture after one transplantation. Gram-stain without counterstain.  
 „ IV Rod with branches from fluid Bordet-medium. Gram-stain with counterstain.  
 „ V  $5 \times 24$  hours' ascites-agar-culture, grown directly from the spleen of v. d. S. Gram-stain with counterstain.  
 „ VI LOEFFLER'S serum-culture transplanted after 12 weeks from original LOEFFLER'S serum-culture, obtained from a gland of patient S.

**Physics.** — “*Measurements on the ultraviolet magnetic rotation in gases.*” By DR. J. F. SIRKS. (Communicated by Prof. KAMERLINGH ONNES.)

(Communicated in the meeting of October 26, 1912).

1. To get an idea of the relative values of the various theories which have been developed to explain magnetic rotation, measurements may be made in the neighbourhood of absorptionbands and -lines in the visible spectrum with a view to ascertain whether the rotation has the same<sup>1)</sup> or opposite sign<sup>2)</sup> on either side of the absorptionband. With perfectly transparent substances one could extend one's observations over a much wider region of the spectrum so as to ascertain if the experimental results obtained in the ultraviolet, for which the rotatory constants are much greater, can be more satisfactorily represented by the one theory than by the other, and if, perhaps, a strong increase in the rotation takes place on approaching the ultraviolet region.

With gases, and in particular with hydrogen, where, on account of their simple molecular structure ordinary refraction of light can well be represented by the assumption of a single kind of ultraviolet electrons<sup>3)</sup>, and for which the value of  $e/m$  may be obtained from the

1) VOIGT, *Magneto- und Elektro-optik* p. 133.

DRUDE, *Hypothese des Hall-effektes*, *Lehrbuch der Optik* p. 429, 1906.

2) DRUDE, *Hypothese der Molekularströme*, *Lehrbuch der Optik* p. 419.

3) ABRAHAM, *Theorie der Elektrizität II*, p. 261, 1908.

magnetic rotation in the manner indicated by SIERTSEMA<sup>1)</sup>, the question arises as to whether ultraviolet measurements would not enable one to ascertain if this value of  $e/m$  is actually constant, and thus justify such a simple assumption for the case of hydrogen. As the ultraviolet magnetic rotation has hitherto been investigated only for solids and liquids<sup>2)</sup>, I was glad to accept the invitation extended to me by Prof. KAMERLINGH ONNES to endeavour to extend SIERTSEMA'S<sup>3)</sup> measurements to the ultraviolet region of the spectrum with the same apparatus as the latter had used.

2. In order to obtain good results from the use of this apparatus absorption of the ultraviolet rays had to be prevented, hence quartz was chosen instead of glass as the material for the covers, lenses and prism, while the canadabalsam-nicols were replaced by GLAN'S air layer nicols.

For preliminary experiments I used a fluorescent eyepiece filled with aesculin solution, but this was found unsuitable on account of the small intensity of the light. When I had a spectrograph at my disposal I was able to photograph the dark rotationband which occurs in the BROCH-WIEDEMANN method and which SIERTSEMA had used for purposes of adjustment, but in the ultraviolet the band was too broad and the spectrum was too feeble to allow the centre to be determined to the desired degree of accuracy. I decided therefore to follow LANDAU and use a half-shadow method.

In this method a half-shadow analyser divides the field into two halves, whose planes of polarisation make a small angle of  $2\delta^\circ$  with each other; if now a rotating substance is placed in the path of the rays between the nicols, and the rays from the analyser are received in a spectroscope, two spectra are formed, one above the other, in which the dark rotationband does not occupy the same position. If the angle of rotation for the position of the band in the one spectrum is  $\alpha^\circ$ , then in the other spectrum the band is at a place where the rotation is  $(\alpha + 2\delta)^\circ$ . At a point at which the rotation is  $(\alpha + \delta)^\circ$ , there is, for a special wavelength, the same intensity in the two spectra. On rotating the polariser the position

<sup>1)</sup> SIERTSEMA, These Proc. Vol. V, p. 413.

<sup>2)</sup> VAN SCHAİK, Proefschrift Utrecht 1882. JOUBIN, Ann. Chim. Phys. S. 6, T. 6, p. 78. 1889. BOREL, Arch. des Sc. Phys. et Nat. Genève, 16, p. 24, 1903. LANDAU Phys. Ztschr. 9, p. 417, 1908. DARMOIS, Ann. Chim. Phys. S. 6, T. 22, p. 247, 495, 1911.

<sup>3)</sup> SIERTSEMA, Versl. K. Ak. v. Wet, 24 Juni 1893, p. 31; 26 Jan. 1895, p. 230; 28 Maart 1896, p. 294; 24 December 1898, p. 280; 27 Mei 1899, p. 4.

of equal intensity of illumination is displaced along the spectrum. When using a discontinuous spectrum (iron arc, or HERAEUS quartz mercury arc) equal intensity has to be obtained between the halves for a definite line of the spectrum. From a series of photographs for different positions of the polariser LANDAU obtained that particular position in which there was equal illumination for a special wave length; the current was then reversed and the series of photographs repeated. Such a method of operating is tedious, but it has the great advantage of giving the required angle of rotation direct from the photographs without the measurements, which are required for determining wavelengths in a continuous spectrum.

3. In order to adapt LANDAU's method to the investigation of gases, the following modifications of SIERTSEMA's apparatus had to be made:

*a.* The polarising nicol had to be replaced by a half-shadow nicol, to which the slit was attached. When the half-shadow was used as analyser, the great length (about 230 cm) of the high pressure tube brought the slit too far from the source, and the light was then too feeble.

*b.* Equal intensities had to be obtained by varying the current, as the half-shadow nicol attached to the rotating end of the experimental tube had to be maintained in a fixed position.

It was now possible, by slightly varying the current for successive photographs, to determine accurately, for different lines of the spectrum, the particular current, at which equal intensities were obtained. These currents are inversely proportional to the rotatory constants, and the constants can be expressed in terms of a standard line as unit.

A preliminary investigation was made to see if it was not possible to arrange the nicols outside the experimental tube. As the quartz covers were ordered of equal but opposite rotations, the measurements would have been simplified by attaching the analyser with a divided circle to the spectroscope, for I should then have been able to read the rotations directly. With the quartz plates placed between the nicols, however, perfect extinction could not be obtained, so that for the determination of VERDET's constant in absolute measure I was obliged to have recourse to a comparison with water, for which the constants have been determined by SIERTSEMA<sup>1)</sup> and LANDAU. It was of advantage then that there was nothing but gas between the nicols, thus eliminating the influence of repeated reflections and of the magnetic rotation in the quartz plates.

4. A diagram of the apparatus is given in Fig. 1.

*L* is a HERAEUS quartz mercury lamp, *A* a collimator, *C* and *D* the coils, *FF'*

<sup>1)</sup> SIERTSEMA. Arch. Néerl. (2) 6. p. 825. 1901.

the high pressure tube, *B* the small rotating endpiece, containing the half-shadow nicol and slit, *E* the large fixed endpiece, containing the analyser, *G* a screw with a wheel, by which with the steel wire *H* and the weight *I* the endpiece *B* may be rotated, *PQ* the spectrograph.

In series with the coils are:

The main switch *A*<sub>1</sub>, two dial resistances *W*<sub>I</sub> and *W*<sub>II</sub> indicating to 0.01 ohm coupled in parallel, a manganin resistance across which is shunted a resistance box

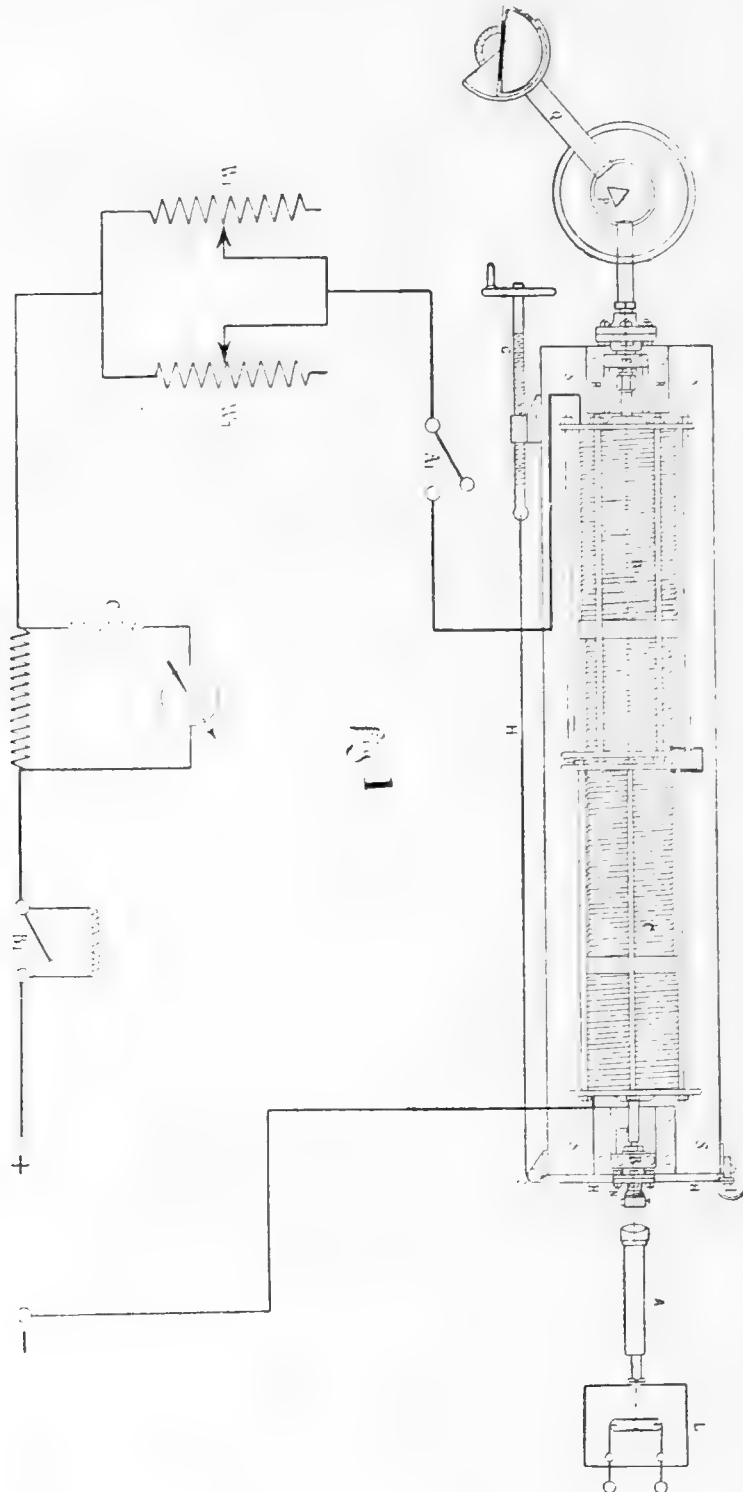


Fig. 1.

in series with a moving coil galvanometer (clock model) by HARTMANN and BRAUN, an auxiliary switch *B*<sub>I</sub> in parallel with a sliding resistance, through which the current is switched before being broken so as to diminish the intensity of the spark.

In the measurements the current varied from 10 to 40 amp. and was obtained from three 60 volt batteries of accumulators, coupled in parallel.

For the absolute determination of VERDET'S constant the current was measured with an ammeter having three ranges (0—2, 0—20, 0—50 amp). This ammeter was calibrated on the potentiometer, and, moreover, when taking the photographs, the variation of the current was so chosen that the pointer of the instrument coincided with the graduations as during the calibration, so that the current is known with certainty to one-tenth of an amp. (one scale division = 0,5 amp.)

The pressure was measured on a SCHÄFFER and BUDENBERG metal manometer with a circular scale of 16 cm diameter, reading up to 150 kg/cm<sup>2</sup> by steps of  $\frac{1}{4}$  kg/cm<sup>2</sup>. The greatest difference between two independent calibrations did not exceed 0,1 kg/cm<sup>2</sup>. We assumed therefore that the pressure is accurate to 0,1 kg/cm<sup>2</sup>.

The manometer was coupled directly to the experimental tube, and, along with it, could be shut off from the rest of the apparatus by means of a tap. The rest of the apparatus consisted of a gascylinder and an airpump (a GAEBDE vacuum kapsel-pump);

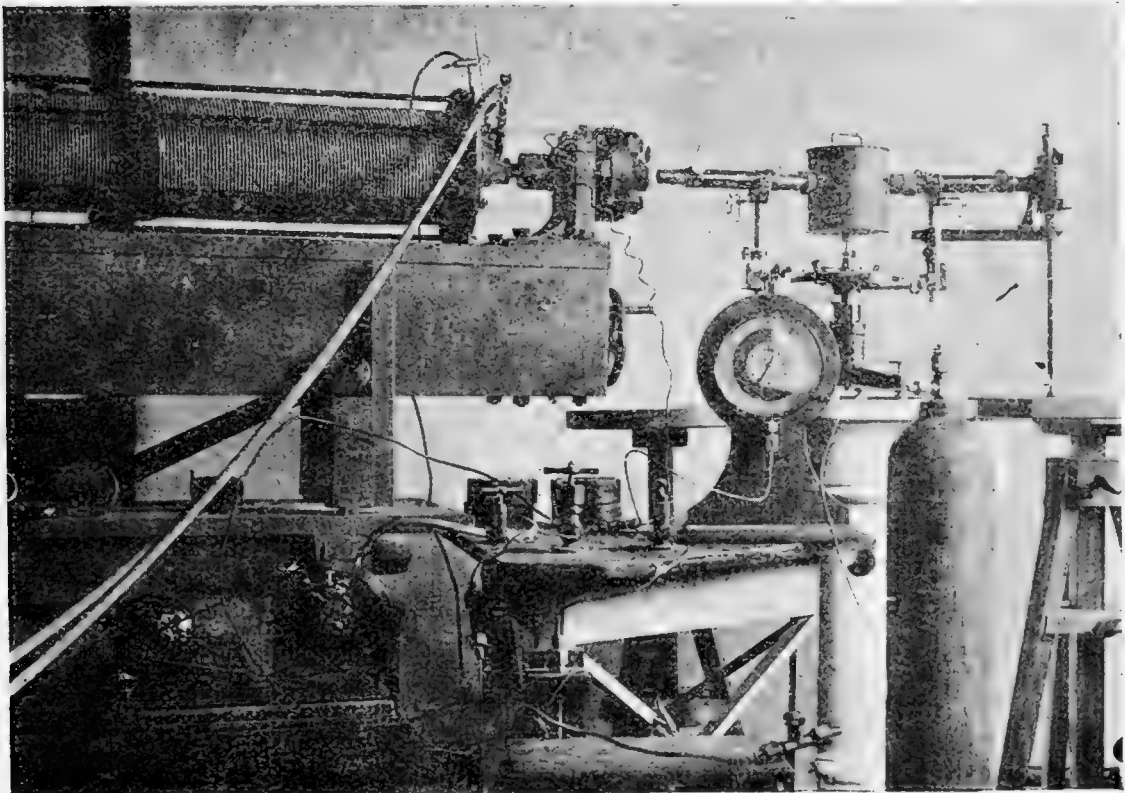


Fig. 2.

there was also an exit tap for the gas in the experimental tube, as it would not have been good for the nicols to expose them to the high pressure for days on end.

To guard against any displacement of the coils, the high pressure taps which were mounted before on the base of the coils, were now placed on a separate table. The temperature of the gas was regulated by that of a water jacket between the coils and the experimental tube. (These details are easily distinguishable in the accompanying photograph of the work room).

5. The following remarks may be made concerning the optical part of the investigation :

The collimator placed in front of the mercury lamp contained a single laevorotatory quartz lens, of 36 cm. focal length for the yellow mercury light, and 3.6 cm. diameter. The breadth of the slit was 1 mm, and its length was reduced by means of a brass plate to 2 mm. so as to prevent troublesome reflection from the inner wall of the experimental tube. A circular opening of 1 mm. diameter was substituted later for this slit.

The quartz covers were 11 mm. thick, and their diameters were 26 and 22 mm. respectively.

The half-shadow (aperture 12 mm. by 12 mm.) with air separation, according to GLAN, had a half-shadow angle of about  $2^\circ$ . It was fixed in a brass mount, and this fitted closely into a brass cover, whose ribbed sides were soldered in a cylindrical tube. The gas had free access to the nicols through the openings, thus removing any possibility of displacement. To enable one to set the separating line of the half-shadow horizontal, the cylindrical tube was arranged so as to rotate in a ring attached to the endpiece. A tube, with a slit 11 mm. long and  $\frac{1}{2}$  mm. wide, perpendicular to the separating line, was attached to the half-shadow half of the nicol.

A GLAN-nicol, aperture 20 mm. by 20 mm. was used as an analyser; it was mounted in the same way so as to rotate in the larger endpiece of the experimental tube. The mount was provided with a circular scale of 180 subdivisions which was used in setting the nicols at a special angle to each other. For the absolute measurements the construction of the nicols was somewhat modified as the water entered the airspace, and the nicols no longer polarised. A brass window ( $\frac{1}{2}$  mm. thick) was cemented between the halves of each nicol, and in this way the space between the nicols was protected on all sides by a layer of cement from ingress of gas or liquid.

As spectrograph was used a Société Genèveise spectrometer with a CORNU quartz prism. The telescope tube contained a single quartz lens, of 36 cm. focal length for yellow mercury light, and of 3.6 cm. diameter. The eye-piece was replaced by a camera, which was constructed in the workshop of the Delft laboratory by the master instrumentmaker Mr. P. VAN DEN AKKER; the accompanying diagram shows the arrangement drawn to a scale of one half :

*B* is a horizontal arm attached to the telescope stand; *C* is a fixed semi-cylindrical brass drum, and *D* a similar semi-cylinder rotating about an axis coincident with the vertical central line of the photographic plate, by means of which it is possible to set the plate at an angle (usually  $50^\circ$ ) to the axis of the camera



tube; *E* is the sliding holder for the dark slide (5,2 by 8,4 cm) and can be raised by means of a vertical screw (not shown) of 1 mm. pitch. The drums were slitted in such a way that only a strip of the sensitive plate 30 mm. long and

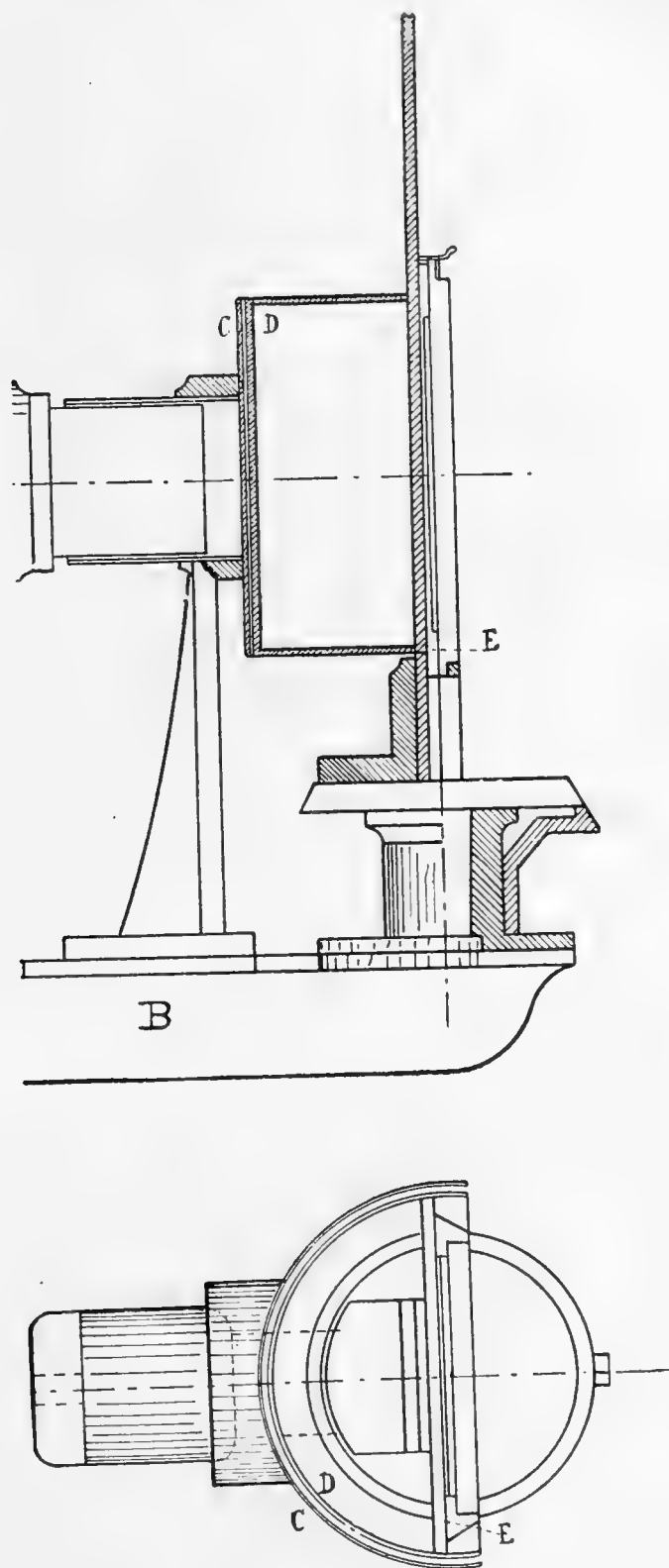


Fig. 3.

3 mm. broad was illuminated at each exposure. The double spectrum formed was about 1.5 mm. broad and was 25 mm. long for the range 4358 *A.U.* to 2805 *A.U.* Nineteen photographs could be taken one below the other on a plate 4.5 cm. by 6 cm. (Lumière Agfa-plates specially sensitive to extreme ultraviolet). The exposures

ranged from 1 to 18 minutes. Parts of the mercury-spectrum were photographed, and the cameratube was usually so adjusted by means of the divided circle of the spectrometer that the mercuryline to be photographed appeared in the middle of the plate. Immediately after the development of the plates it was examined in which photo the intensities of the halves were equal for a special line. This could be properly observed only when the illumination of the half-shadow slit was uniform, and for this reason the mercurylamp had to be kept burning in a vertical position.

On account of absorption photographs were taken

for oxygen	up to and including	2654 <i>A.U.</i>
„ hydrogen	„ „ „ „	2378 „
„ carbon-dioxide	„ „ „ „	2482 „

For ultraviolet absorption by oxygen I find it stated<sup>1)</sup> that LIVEING and DEWAR found absorption from 2745 *A.U.* upwards in a tube 165 cm. long at a pressure of 85 atm. and from 3360 *A.U.* upwards in a tube 18 m. long at a pressure of 80 atm. In my experiments the oxygen-column of 230 cm. at a pressure of 80 kg/cm<sup>2</sup> just let the line 2805 *A.U.* through and no more, while for a pressure of 40 kg/cm<sup>2</sup> the limit of absorption was 2654 *A.U.*

6. Measurements of the rotatory dispersion were commenced with :

### *Oxygen.*

Before the experimental tube was filled and closed, the nicols were set at an angle previously calculated. The cameratube was then replaced by a telescope in order to ascertain what current strength gave equal intensities of the halves of the green or the violet mercury line. By a slight torsion of the experimental tube equal intensity was usually obtained for the blue-violet line 4358, with a current of about 35 amp, a gas pressure of 85 kg/cm<sup>2</sup> and an angle of 92° between the nicols. The necessary current strengths for the ultraviolet lines could then be calculated roughly by extrapolation from the dispersionformulae given by SIERTSEMA. If  $I$  is the value of the current thus calculated, photographs were usually taken with currents of from  $(I - 2)$  and to  $(I + 2)$  amp. and a series of careful exposures were then made at intervals of  $\frac{1}{40}$  or  $\frac{1}{50} I$  amp. between the values of  $I$  given by the first photographs. A current of 1 amp. gave a galvanometerdeflection of 1 cm. so that with the currents used a change of 3 to 8 mm. in the galvanometerdeflection could just be distinguished on the negative by an appreciable difference in darkness.

As the original negatives were too weak for reproduction, I prefer to give a drawing of a series of 7 photographs of a portion of the mercuryspectrum (4047—2755 *A.U.*) with hydrogen at 19°,5 and

<sup>1)</sup> KAYSER, Handbuch. Band III. p. 357.

76 atm.<sup>1)</sup>. Equal intensities for the line 3130 (in the centre of the plate) occur between the 4<sup>th</sup> and 5<sup>th</sup> exposure from above. The variation of the current was  $\frac{1}{2}$  amp.

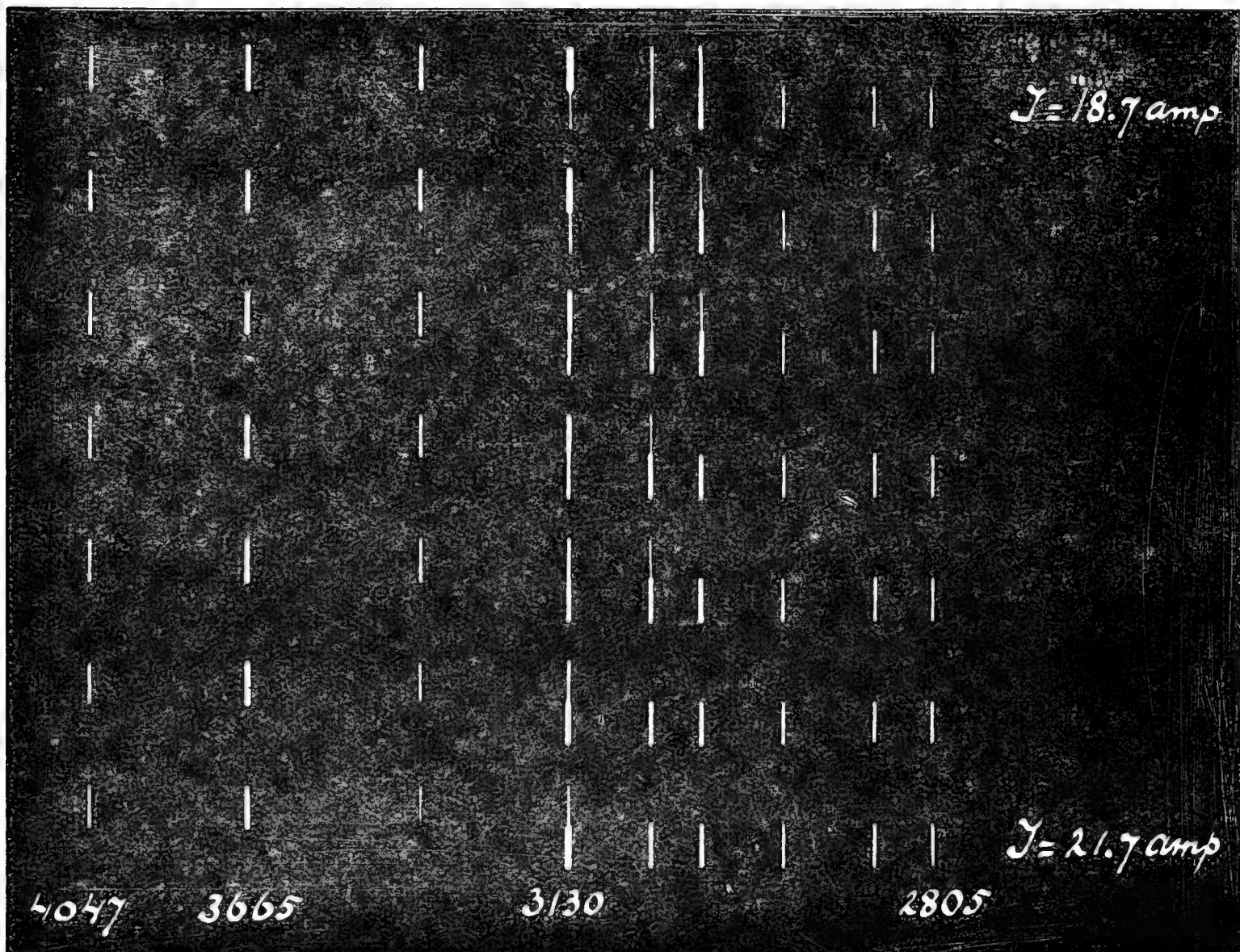


Fig. 4.

As the ammeterreadings, or the galvanometerdeflections corrected to angular deflections, are, for constant gasdensity, inversely proportional to the required VERDET's constants, the relative rotatory constants can be calculated from such photographs; in this the constant for the violet line 4358 A.U. is usually chosen as unity. The relative rotation is then obtained from:

$$\rho = \frac{R_\lambda}{R_0} = \frac{I_0}{I_\lambda} = \frac{\alpha_0}{\alpha_\lambda}$$

<sup>1)</sup> The line 2805 is the second from the right, not the first as is erroneously shown in the figure. Horizontal distances are magnified four times, and vertical distances about seven times. Differences in intensity are indicated by differences in breadth.

in which  $R_0$  is VERDET'S constant,  $I_0$  is the current in amp,  $\alpha_0$  is the corrected galvanometerdeflection for the wavelength 4358 A.U., and  $R_\lambda$ ,  $I_\lambda$  and  $\alpha_\lambda$  relate to the other mercury lines. As, owing to small leaks and to temperature fluctuations, the readings of the manometer did not remain perfectly stationary, the dispersion was calculated from

$$\rho = \frac{R_\lambda}{R_0} = \frac{\alpha_0 d_0}{\alpha_\lambda d_\lambda} = \frac{\alpha_0 p_0 (1 + \beta t_\lambda)}{\alpha_\lambda p_\lambda (1 + \beta t_0)} = \frac{\alpha_0 p_0}{\alpha_\lambda P_\lambda},$$

in which  $d_0$  is the density,  $p_0$  the pressure and  $t_0$  the temperature of the gas during the measurement with the line 4358, the subscript  $\lambda$  denotes the other wavelengths,  $\beta$  is the pressurecoefficient (taken from AMAGAT'S observations), and  $P_\lambda$  is equal to  $p_\lambda \{1 + \beta (t_0 - t_\lambda)\}$ .

Since  $P_\lambda$  does not differ much from  $p_0$ , deviations from BOYLE'S law need not be taken into account. For the reduction of the observations at the lower pressure from 2805 to 2654 A.U. the rotation for the line 2805 was first taken to be unity, and the relative dispersion was then obtained by multiplication by  $\frac{R_{2805}}{R_0}$ .

The oxygen used was supplied by the "Oxygenium" Company, Schiedam. It was analysed in a HEMPEL absorptionbulb filled with copper gauze, moistened with a solution of ammonia and ammonium carbonate. For the gas with which the most reliable results were obtained, 97 % of oxygen was found.

The following table is from the photographs, obtained on the 21<sup>st</sup> to the 25<sup>th</sup> of May :

T A B L E I.

$\lambda$ in A.U.	pressure in atm.	temp. in °C.	galv. deflect. mm.	$\rho$
4358	83.8	17.4	335.9	1.00
4047	83.8	17.2	304.9	1.10
3665	83.25	17.5	258.2	1.31
3130	84.9	16.9	184.2	1.79
2805	82.5	17.4	152.3	2.24
2805	40.9	16.7	314.1	—
2755	41.3	17.1	301.9	2.31
2654	41.05	16.5	280.1	2.50

The pressurecoefficient was taken to be 0.0046 for an initial pressure of 84 atm. and 0.0042 for a pressure of 41 atm. These values were obtained by extrapolation from AMAGAT's observations <sup>1)</sup>).

### *Hydrogen.*

7. The first series of measurements were made with double purified hydrogen, supplied by the "Oxygenium" Company; analysis in a HEMPEL explosionbulb showed no impurity. With a view to absolute determinations measurements were subsequently made with a cylinder of very pure hydrogen which had been prepared in the Leiden laboratory by freezing out the impurities at low temperature.

Measurements dated 24<sup>b</sup> to 29<sup>b</sup> of May with the first gas gave the following results:

T A B L E II.

$\lambda$ in A.U.	pressure in atm.	temp. in °C.	galv. deflect. mm.	$R_{\lambda}/R_{4047}$
4047	54.1	15.8	373.8	1.00
3665	56.8	15.2	288.1	1.23 <sup>5</sup>
3130	57.1	14.9	197.1	1.79
2805	52.8	15.7	159.6	2.40
2654	57.8	15.9	126.9	2.75 <sup>5</sup>
2535	56.1	16.5	115.2	3.14
2482	56.4	16.4	107.0	3.35 <sup>5</sup>

The nicols were set beforehand at an angle of 92°. The exposures varied from 1.5 to 10 minutes. The pressurecoefficient was taken to be 0.0037 and no correction was applied for deviations from BOYLE'S law.

A higher pressure was obtainable with the Leiden hydrogen, and the nicols were accordingly set at an angle of 92°.5 for that series of measurements. Currents were measured with the ammeter already described. (range 0 to 50 amp, 1 scale division = 0,5 amp).

The exposure for the last two ultraviolet lines 2399 and 2378 A.U. was 18 mts; the current was kept constant at 10 amp. for an hour. On account of the heating of the coils not more than three exposures could be made in any one series. The following are the results of these measurements:

<sup>1)</sup> WÜLLNER. Experimentalphysik. 5te Aufl. Band II. Tab. p. 138.

T A B L E III.

$\lambda$ in A.U.	pressure in atm.	temp. in °C.	amp.	$\rho$
4358	93.85	18.6	35.74	1.00
4047	93.9	18.3	30.18	1.18
3665	90.0	18.7	25.65	1.45 <sup>5</sup>
3130	88.1	17.9	17.70	2.14 <sup>5</sup>
3130	76.0	19.5	20.45	—
2805	75.2	19.8	15.69	2.83
2654	75.5	19.7	13.44	3.29
2535	74.9	20.9	12.19	3.67
2482	75.0	20.5	11.44	3.90 <sup>5</sup>
2399	74.7	19.3	10.44	4.27
2378	74.8	19.3	10.19	4.37

By calculating values of  $R_\lambda/R_{4047}$  from these measurements we can compare the results obtained with the Leiden and with the Oxygenium hydrogen:

T A B L E IV.

$\lambda$ in A.U.	$R_\lambda/R_{4047}$ Leiden	$R_\lambda/R_{4047}$ Oxygenium
4047	1.00	1.00
3665	1.23	1.23 <sup>5</sup>
3130	1.81 <sup>5</sup>	1.79
2805	2.39	2.40
2654	2.78	2.75 <sup>5</sup>
2535	3.10 <sup>5</sup>	3.14
2482	3.30	3.35 <sup>5</sup>

As the photographs for the last ultraviolet lines were much sharper for the Leiden hydrogen, I have used the values obtained with it for the construction of the dispersion curves.

*Carbon-dioxide.*

8. For this the rotatory constants are greater than for the other gases. The measurements were made at a pressure of 27 atm. as at higher pressures small temperaturefluctuations gave rise to currents in the gas, which rendered the image of the slit indistinct.

Commercial carbon-dioxide was used after purification by distillation; analysis in an absorptionbulb, filled with iron gauze and potassium-hydroxide, showed 96% CO<sub>2</sub>.

The results of the experiments are here given:

T A B L E V.

$\lambda$ in A.U.	pressure in atm.	temp. in ° C.	galv. deflect. mm.	$R_\lambda/R_{4047}$
4047	25.35	16.1	336.1	1.00
3665	27.3	17.5	277.9	1.225
3130	27.3	17.5	189.9	1.79
2805	27.2	17.2	149.8	2.275
2654	27.2	16.5	129.6	2.615
2535	27.3	16.2	114.6	2.95

Exposures ranged from 1.5 to 10 mts. An additional series of photographs of the green and the blue-violet mercury lines was also made upon Agfa-chromatic plates in order to afford a comparison with SIERTSEMA's results. The correspondence was found to be very good:

T A B L E VI.

$\lambda$ in A.U.	$R_\lambda/R_{5461}$	$R_\lambda/R_{5461}$ (after SIERTSEMA)
5461	1.00	1.00
4358	1.605	1.60
4047	1.87	1.87

*Determination of the absolute rotatory constants.*

9. It has been mentioned already that the arrangement of the apparatus for the half-shadow method does not allow of a direct measurement of the angle of rotation, so that a calibration with water is necessary for an absolute determination of the rotatory constants. If the rotatory constant for the wave-length  $\lambda$  at a definite pressure and temperature is  $R_H$  for hydrogen and  $R_W$  for distilled water and if the currents used for the two photographs were  $I_H$  and  $I_W$  amp. respectively, then

$$R_H = \frac{I_W}{I_H} R_W.$$

In this formula the currents must be known with the same relative accuracy. As the rotation by water for the mercuryline 4358 A.U. is about 25,3 times greater than for hydrogen(100 kg/cm<sup>2</sup> 17.°5), the ammeter ranges used were 0 to 2 and 0 to 50 amp. After filling the experimental tube with water I found, contrary to expectation, that the 230 cm. column transmitted the ultraviolet only up to the wavelength 3665 A.U., while LANDAU with a waterlayer of 1 cm. was still able to obtain photographs of the iron line 2496 A.U. I finally used only the line 4358 for these measurements. The exposures were two minutes for hydrogen and five for water. On account of the repeated fillings of the experimental tube the pressure obtainable from the Leiden cylinder of hydrogen sank to 75 kg/cm<sup>2</sup>, so that the currents used for the gas were about 34 times those required for the water photographs.

In this way I obtained for

Hydrogen (73.9 atm. 16°.9.)  $I_H = 37.72$  amp.

Distilled water  $I_W = 1.145$  amp.

According to SIERTSEMA  $R_W = 0.02495'$  for  $\lambda = 4358$ . From my measurements we may calculate  $I_H = 32.88$  amp. for a pressure of 85 kg and a temperature of 9°.5, whence it follows, that  $R_H(85$

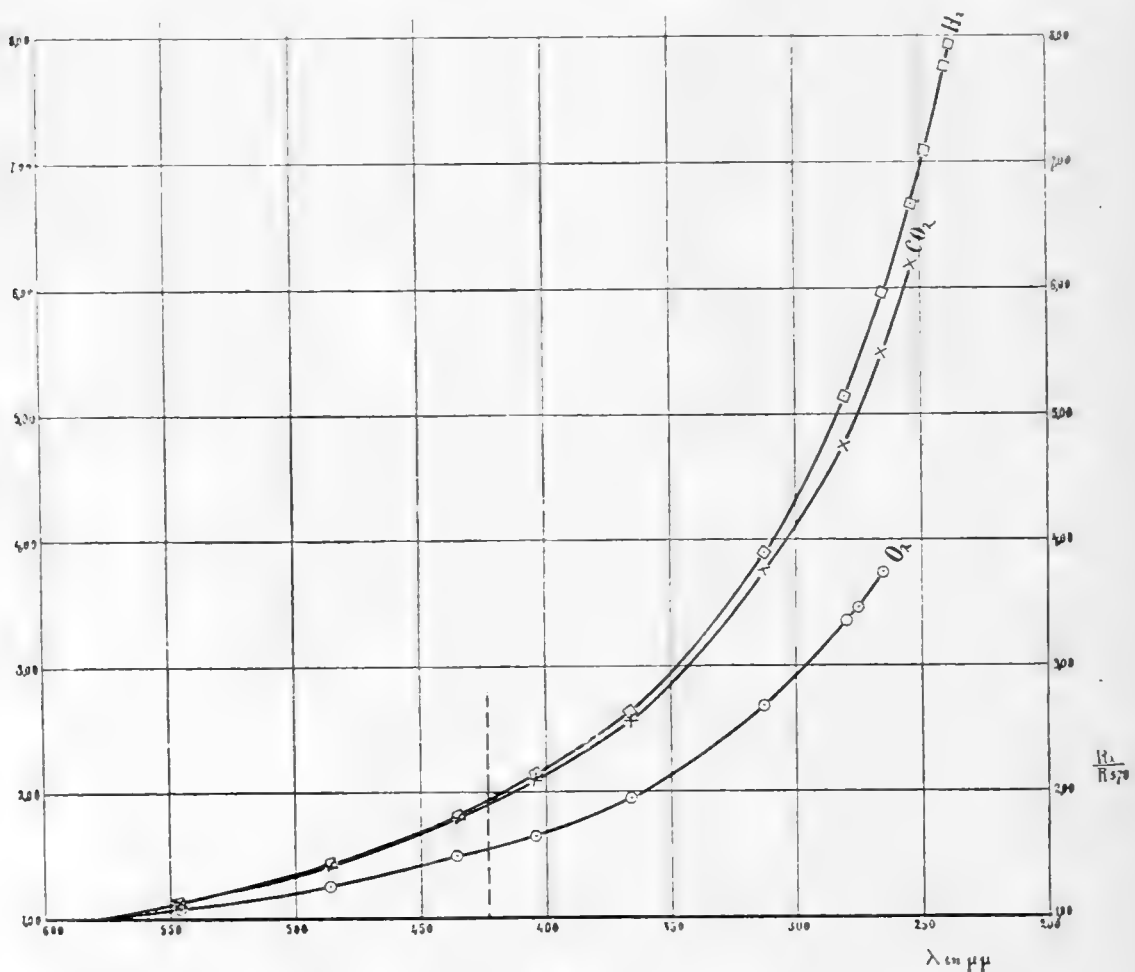


Fig. 5.



$\text{kg/cm}^2 \ 9^{\circ}.5) = (869 \times 10^{-6})'$ . This agrees well with the value given by SIERTSEMA:  $(863 \times 10^{-6})'$ .

10. This led me to unite my results for the three gases with SIERTSEMA's, and to plot the dispersioncurve for each for the visible and ultraviolet regions. The rotatory constant for the yellow mercuryline (mean wavelength 5780 A.U.) was taken to be unity; along the axis of abscissae are plotted wavelengths in  $\mu\mu$ , and along the axis of ordinates the following relative rotations:

T A B L E VII.

$\lambda$ in $\mu\mu$	$R_{\lambda}/R_{578}$		
	Oxygen	Carbon dioxide	Hydrogen
578	1.00	1.00	1.00
546	1.08	1.12 <sup>5</sup>	1.12 <sup>5</sup>
486	1.26 <sup>5</sup>	1.43 <sup>5</sup>	1.44
436	1.50	1.80 <sup>5</sup>	1.81 <sup>5</sup>
404.5	1.65 <sup>5</sup>	2.10	2.15
366.5	1.96 <sup>5</sup>	2.57	2.64
313	2.69 <sup>5</sup>	3.76	3.90
280.5	3.36 <sup>5</sup>	4.77 <sup>5</sup>	5.14
265.5	3.75 <sup>5</sup>	5.49	5.97 <sup>5</sup>
253.5		6.19 <sup>5</sup>	6.67
248			7.09
240			7.76
238			7.94

The dotted line at 423  $\mu\mu$  gives the limit of SIERTSEMA's observations.

It is to be remarked that the oxygen-curve deviates considerably from those for the other gases, but that there is no sudden change as the ultraviolet absorptionregion is approached, and that the difference between hydrogen and carbon-dioxide begins to be good appreciable in the ultraviolet region.

On the assumption that ultraviolet refraction in hydrogen satisfies a formula of the type

$$n^2 = A + \frac{B}{\lambda^2 - \lambda_m^2}$$

in which  $\lambda_m$ , the wavelength of the ultraviolet free vibration, is taken to be  $0,087 \mu$ <sup>1)</sup>, the following values have been calculated for  $e/m$ :

$\lambda$ in $\mu\mu$	$e/m \times 10^{-7}$ for $H_2$ (85 kg 9°5)
589	1.77
405	1.78
313	1.81
265	1.85 <sup>5</sup>
248	1.86
238	1.87 <sup>5</sup>

The increase here found for  $e/m$  does not accord with the assumption of a single ultraviolet free vibration.

I must, in conclusion, offer my warmest thanks to Prof. Dr. H. KAMERLINGH ONNES for inviting me to undertake this investigation and for placing the necessary high-pressure apparatus at my disposal and also to Prof. Dr. L. H. SIERTSEMA for granting such excellent facilities for the work and for the unflagging interest with which he has followed the investigation.

*Delft*, October 1912.

*Physical Laboratory of the  
Technical University.*

1) SIERTSEMA and DE HAAS. These Proc. Vol. XIV. p. 603.





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