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KONINKLIJKE AKADEMIE  
VAN WETENSCHAPPEN  
-- TE AMSTERDAM --

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JOHANNES MÜLLER :—: AMSTERDAM  
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# C O N T E N T S.



	Page
Proceedings of the Meeting of December 30, 1914 . . . . .	873
»    »    »    »    »    January 30,    1915 . . . . .	945
»    »    »    »    »    February 27,    »    . . . . .	1075
»    »    »    »    »    March 27,    »    . . . . .	1135
»    »    »    »    »    April 23,    »    . . . . .	1203





KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING  
of Wednesday December 30, 1914.

VOL. XVII.

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

*Secretary:* Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Woensdag 30 December 1914, Dl. XXIII).

CONTENTS.

- H. DU BOIS: "The universality of the ZEEMAN-effect with respect to the STARK-effect in canal-rays", p. 873.
- J. J. VAN LAAR: "The calculation of the molecular dimensions from the supposition of the electric nature of the quasi-elastic atomic forces." (Communicated by Prof. H. A. LORENTZ), p. 877.
- J. K. A. WERTHEIM SALOMONSON: "Exaggeration of Deep Reflexes." p. 885.
- W. H. KEESOM and H. KAMERLINGH ONNES: "The specific heat at low temperatures. I. Measurements on the specific heat of lead between 14° and 80° K. and of copper between 15° and 22° K." (Communicated by Prof. H. KAMERLINGH ONNES). p. 894.
- C. WINKLER: "A case of occlusion of the arteria cerebelli posterior inferior." p. 914.
- ERNST COHEN and G. DE BRUIN: "The metastability of the Metals in consequence of Allotropy and its significance for Chemistry, Physics and Technics." III, p. 926.
- JAN DE VRIES: "Characteristic numbers for nets of algebraic curves." p. 935.  
Erratum, p. 944.

**Physics.** — "*The universality of the ZEEMAN-effect with respect to the STARK-effect in canal-rays.*" By H. DU BOIS. (Communication from the BOSSCHA-Laboratory).

(Communicated in the meeting of November 28, 1914).

Notwithstanding several efforts <sup>1)</sup> no one had succeeded in demonstrating the smallest influence of electrostatic fields on spectral lines until STARK <sup>2)</sup> observed such a specific effect for lines emitted by the

<sup>1)</sup> See G. F. HULL, Proc. Roy. Soc. **78** p. 80, 1907. P. ZEEMAN, These Proc. **19** p. 957, 1911; **20** p. 731, 1911. F. PASCHEN & W. GERLACH, Phys. Ztschr. **15** p. 489, 1914.

<sup>2)</sup> J. STARK and his collaborators, Sitz.ber. Berl. Akad. **47** p. 932, 1913; Ann.

canal-rays of hydrogen, helium and lithium. In his experiments the electric field,  $\mathfrak{E}$ , reached values of more than 150 electrostatic units, viz.  $\mathfrak{E}_m$  in electromagnetic units was more than 45 kilovolt/cm; the largest separation surpassed  $2 \mu\mu$  for  $H_\gamma$  ( $\lambda = 434,1 \mu\mu$ ).

Starting from the theoretical equivalence of  $\mathfrak{E}_m$  and the vector-product  $[\mathfrak{B} \mathfrak{H}]$  W. WIEN<sup>1)</sup> then presumed an analogous specific magnetic separation of spectral lines of hydrogen canal-rays and experimentally verified this. In his experiments the maximum velocity in the canal-rays,  $\mathfrak{B}$ , reached a value of 7700 km. per second; while the magnetic field  $\mathfrak{H}$  was about 17 kilogauss. The separation observed for  $H_\gamma$  was of the order of  $0,5 \mu\mu$ , i. e. very much larger than that of the ordinary ZEEMAN-effect, for which the normal separation in this field would amount to about  $0,03 \mu\mu$  only.

As far as we can now already judge, we have here two separate, without doubt closely connected, phenomena, which are both proportional with the field and which appear to depend on the velocity of the charges. With an extremely sensitive method PASCHEN and GERLACH sought for an electric effect ( $\mathfrak{E} = 15$  kilovolt/cm) in mercury vapour; but in vain. From this they rightly conclude, that there is no question here of an electric analogon of the real ZEEMAN-effect. For this is generally shown by many lines of emission, absorption and fluorescence of vapours and selective crystals: the unsensitiveness of certain lines moreover may be only apparent ( $d\lambda < 0,002 \mu\mu$  say).

As early as 1899 this problem was treated theoretically by VOIGT<sup>2)</sup>; according to him an electro-optic displacement or separation probably would occur, though maybe a very small one, proportional with  $\lambda^5 \mathfrak{E}^2$ . Therefore it would be favourable for observation to choose these two factors as large as possible. Recently, before the publication of WIEN'S experiments however, WARBURG and SCHWARZSCHILD<sup>3)</sup> have developed formulae, the former starting from the theory of quanta, the latter by means of purely attractory considerations. SCHWARZSCHILD

d. Phys. **43** p. 965—1045, 1914; Phys. Ztschr. **15** pp. 215, 265, 1914; Verh. D. Phys. Ges. **16** p. 304, 1914. Elektr. Spektr. anal. chem. Atome, Leipzig 1914. A. Lo SURDO, Rend. Acc. Lincei (1) **23** p. 143, 1914; Phys. Ztschr. **15** p. 122, 1914. H. WILSAR, Gött. Nachr. **9** p. 20, 1914. H. LUNELUND, Ann. d. Phys. **45** p. 517, 1914.

<sup>1)</sup> W. WIEN, Sitz. Ber. Berl. Akad. **48** p. 70, 1914.

<sup>2)</sup> W. VOIGT, Wied. Ann. **69** p. 297, 1899; Ann. d. Phys. **4** p. 197, 1901; Arch. Néerl. (2) **5** p. 366, 1901. Magneto- und Elektrooptik pp. 357, 380, Leipzig 1908; Gött. Nachr. **9** p. 1, 1914; Ann. d. Phys. **45** p. 461, 1914.

<sup>3)</sup> E. WARBURG, Verh. D. Phys. Ges. **15** p. 1259, 1913. K. SCHWARZSCHILD, ibidem **16** p. 29, 1914.

finds a separation proportional with  $\lambda^{7/5}\mathcal{E}$ , WARBURG however a broadening proportional with  $p^2\lambda^2\mathcal{E}$ , where  $p$  denotes the number of the series. The formulae of GARBASSO, GEHRCKE and BOHR<sup>1)</sup> differ from that of WARBURG in so far only as, besides other numerical factors, they contain  $p^2\lambda\mathcal{E}$  as a parameter. The simultaneous influence of a magnetic and an electric field was treated both theoretically and experimentally by ZEEMAN, STARK, GARBASSO and GEHRCKE<sup>2)</sup>.

Luminescent vapours always more or less cause a migration of electricity which in the experiments of STARK e.g. amounted to several milliampères. It seemed to me interesting to examine the influence of a purely dielectric displacement. As ZEEMAN already pointed out (loc. cit.) for this purpose we must consider an insulating, selectively absorbing crystal. Among the series of substances formerly tested ruby will be found a very good material for such experiments<sup>3)</sup>. It is not hygroscopic, it insulates extremely well and has an ordinary index of refraction  $n_\omega = 1,769$  (for  $\lambda = 589 \mu\mu$ ), and  $n_\omega^2 = 3,13$ . Considering the analogy with quartz we may expect the dielectric constant to be much larger still. In connection with this research SELÉNYI<sup>4)</sup> already investigated in the BOSSCHA-laboratory the influence of an elastic deformation on the absorption lines of ruby. For a pressure of 150 kg/mm<sup>2</sup> however he could not detect an appreciable effect, at least no more than 0,02  $\mu\mu$ .

The electrostatic experiment had to be delayed several years by the difficulty of obtaining artificial rubies of sufficient size, because of a monopolistic tendency in their preparation. Only recently I was kindly furnished with sufficient material. From this two disks were cut, about 3 mm thick, one  $\perp$  and one  $\parallel$  the crystal axis. By means of sealing wax these were fixed within ebonite plates of the same thickness. Unsymmetrical contraction by sudden cooling or high electrostatic tension (during a short time) did not appreciably injure these slides. To both sides of the dielectric plates small brass disks were fixed. In the middle of these a slit was made so that an eventual longitudinal effect might be observed. Extremely thin tubes of German silver fitted in glass tubes connected the brass

<sup>1)</sup> A. GARBASSO, Phys. Ztschr. **15** pp. 123, 310, 1914. E. GEHRCKE, Phys. Ztschr. **15** pp. 123, 198, 344, 839, 1914; Verh. D. Phys. Ges. **16** p. 431, 1914. N. BOHR, Phil. Mag. (6) **27** p. 506, 1914.

<sup>2)</sup> P. ZEEMAN, These proceedings, **14** p. 2, 1911. J. STARK, Verh. D. Phys. Ges. **16** p. 327, 1914. A. GARBASSO, Phys. Ztschr. **15** p. 729, 1914. E. GEHRCKE, Phys. Ztschr. **15** p. 839, 1914.

<sup>3)</sup> H. DU BOIS and G. J. ELIAS, These proceedings, **10** pp. 578, 734, 839, 1908; Ann. d. Phys. **27** p. 233, 1908; **35** p. 617, 1911; **45** p. 1160, 1914.

<sup>4)</sup> P. SELÉNYI, Verh. D. Phys. Ges. **15** p. 290, 1913.

disks with a WIMSHURST electrical machine, giving a tension of more than 90 kilovolt. A vacuum-glass was half filled with liquid air and covered with an ebonite stopper, which was perforated for the glass tubes. Though the moisture in the laboratory hardly ever exceeded 30 to 40%, the whole apparatus was placed under the case of an exsiccator. In this way the ruby could for some time endure a tension of about 60 kilovolt, that is of  $60/0,3 = 200$  kilovolt/cm. = 667 electrostatic units.

The absorption lines, especially the two strongest lines  $R_2$  and  $R_1$  in the red (691,8 and 693,2  $\mu\mu$ ) were observed in the first order of a concave grating (radius 181 cm., 5684 rulings per cm.), which was mounted in the ordinary way. 1 mm corresponded fairly well to 1  $\mu\mu$ , so that a change of the order of 0,005  $\mu\mu$  could not escape observation. No influence of electrification could however be detected; in any case the displacement or separation is less than one hundredth part of the magnetic longitudinal effect in a field of 50 kilogauss. For the latter we formerly found the values:

	$R_2$	$R_1$
Axis $\parallel$ field; triplets with extreme separation	$\delta\lambda: 0,37$	$0,43 \mu\mu$
Axis $\perp$ field; quadruplets „ „ „	$\delta\lambda: 0,62$	$0,62 \mu\mu$

Probably an interferential method might give a sharper criterion than the rather small dissolving power of the grating. Such experiments might be made with the corresponding fluorescence spectrum of the ruby at a very low temperature; they must be delayed however until a more sunny season of the year. As this subject is of great importance it seems to me interesting even to determine the minimum limits in negative researches.

I also made experiments with the neodymnitrate-hexahydrate ( $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) from the series of the rare earths. A natural monocline plate about 1 mm thick was cut  $\perp$  to one of the axes and in the manner above mentioned mounted between two very thin glass plates by means of Canada balsam. Observations were made at  $-190^\circ$  on the group of bands in the red, numbered from I to VIII in a former paper (loc. cit. § 32). On account of the smaller thickness of this slide the electric field was even stronger here than in the case of the ruby; but again no perceptible influence on the absorption bands was found. Now in a magnetic field the bands VII and VIII (676,6 and 677,2  $\mu\mu$ ) give doublets the separation of which reaches the largest observed value viz.  $\delta\lambda = 1,0$  and  $1,1 \mu\mu$  for 50 kilogauss.

For the sake of completeness I repeated the experiment with an

alcoholic solution of the salt in a trough, which contained platinum electrodes 2 cm distant from each other. A potential difference of 100 volt was applied. At 18° the current density was 75 milliamp./cm<sup>2</sup> and in the viscous solution just above the freezing point of aethyl-alcohol (−118°) 30 milliamp./cm<sup>2</sup>. I also worked with a dilute solution in amyl-alcohol (−134°). With a spectral apparatus of very great dispersion I observed in this case considerably broadened and diffuse absorption bands, the aspect of which did not change when the current was made. It must be remarked however that under these circumstances the velocity of the negative ion is very small as yet.

**Physics.** — “*The calculation of the molecular dimensions from the supposition of the electric nature of the quasi-elastic atomic forces*”. By DR. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of October 31, 1914).

1. In four papers<sup>1)</sup>, in which some new relations between the critical quantities were given, I have also tried to determine the form of the function  $b = f(v; T)$ . While the dependence of  $b$  on the volume appeared to be pretty intricate — that namely the found relations at the critical point and at the same time the limiting condition at  $v = v_0$  be satisfied — the dependence on the temperature could be given by a very simple relation, namely (see III, p. 1053, formula (36)):

$$\frac{b_g - (b_0)}{(b_0)} = 0,041 \sqrt{T}, \quad . . . . . (1)$$

in which  $(b_0)$  represents the value of the limiting volume  $b_0 = v_0$ , extrapolated from the direction of the so-called straight diameter at  $T_k$ . This formula was an extension of that which was found at the critical point, namely (loc. cit. p. 1051):

$$\frac{b_k - (b_0)}{(b_0)} = 2\gamma_k - 1 = 0,038 \sqrt{T_k}, \quad . . . . . (2)$$

in which  $\gamma_k$  is the coefficient of direction of the “straight diameter” in the neighbourhood of the critical point. The table (p. 1052) calculated to support this relation may be reproduced here.

<sup>1)</sup> These Proc. of March 26, April 23, May 29 and Sept. 26, 1914.

	$T_k$	$\sqrt{T_k}$	$2\gamma_k - 1$	$\gamma_k$ calculated	$\gamma_k$ found
Helium	5.2	2.28	0.0866	0.543	$\pm 0.56$
Hydrogen	32.3	5.68	0.2158	0.608	0.604
Argon	150.65	12.27	0.4763	0.738	0.745
Xenon	289.7	17.02	0.6468	0.823	0.813
Acetylene	308.5	17.56	0.6673	0.834	0.858
Isopentane	460.9	21.47	0.8159	0.908	0.914
Fluorbenzene	559.6	23.66	0.8991	0.950	0.933

We have already repeatedly pointed out, that both the form of the function  $b = f(v)$ , and the form of the temperature function  $b = f(T)$  suggest that the change of  $b$  chiefly, probably even exclusively, corresponds to a *real* volume change of the molecules, and that an apparent change in consequence of the partial overlapping of the so-called distance spheres must be rejected. (See among others IV, p. 464).

That such an apparent change loses all foundation in consequence of the non-existence of the relation  $b = 4m$ , has been conclusively proved by me in my opinion in a later article (These Proceedings of Nov. 7, 1914). We found there namely (see p. 611), that in consequence of the influence of the (infinitely slight) quasi-association at  $v = \infty$  the quantity  $b$  must be diminished by the *finite* quantity  $R : C$ . ( $C =$  the "constant" of the quasi-association). Considerations of another nature made it probable that  $b$  must, indeed, be identified in all cases with the real molecular volume  $m$ , at most increased by a certain influence sphere.

2. We have already seen that the found temperature relation agrees perfectly with that given by a formula drawn up by VAN DER WAALS already much earlier for the variability of  $b$ , viz.

$$[p + \frac{a}{v^2} + A(b - b_0)](b - b_0) = fRT, \quad . . . . (3)$$

in which  $A$  represents the (spacial) constant of the quasi-elastic atomic forces, which atomic forces were put proportional to the increase of volume  $b - b_0$ . The quantity  $f$  is a coefficient which depends on the number of degrees of freedom.

After substitution of  $RT : (v - b)$  for  $p + \frac{a}{v^2}$ , and elimination of  $A$  and  $T$ , formula (3) appeared, however, *not* to satisfy the relation  $b = f(v)$  found by us. (See particularly II, p. 930 in con-

nection with II, p. 931 and III, p. 1048, where the probable form for this relation was given). If, however, we do not enter into a further consideration of the extra-molecular part  $(\rho + a/v^2)(b - b_0)$ , and for the present examine only the intra-molecular part  $A(b - b_0)^2$ , we can, in connection with some plausible supposition concerning  $A$ , examine what conclusions might be derived from it with regard to the absolute size of the molecules, and whether the found dimensions agree with the molecular dimensions derived from other data.

The simplest supposition concerning  $A$  is, that the quasi-atomic forces are brought about under the influence of two elementary-charges  $e$ , so that for the (linear) constant of the atomic forces, following LINDEMANN (see among others Conseil SOLVAY, German edition of 1914, p. 286; and also pp. 316—317, as far as the derivation from THOMSON'S atom model is concerned),

$$F_0 = \frac{Nne^2}{d^3} \dots \dots \dots (4)$$

may be written, in which  $N$  represents the number of molecules per gr. mol.,  $n$  the valency of the atoms, sub-atoms or atom groups, and  $d$  the equilibrium distance of the charges. If further the deviation is  $\sigma$ , the atomic force for not too great values of  $\sigma$  is represented by

$$F = F_0 \sigma,$$

and the term of the energy corresponding to  $A(b - b_0) \times (b - b_0)$  by  $F_0 \sigma \times \sigma$ .

According to (4) we can now write for  $F_0 \sigma^2$ :

$$F_0 \sigma^2 = \frac{Nne^2}{d^3} \sigma^2, ^1)$$

or also when  $s_0$  is the smallest diameter of the molecules (i.e. with a deviation of the atoms  $\sigma = 0$ ):

$$F_0 \sigma^2 = \frac{Nne^2}{s_0^3} \left(\frac{s_0}{d}\right)^3 \sigma^2.$$

If we assume a spherical shape for the molecules (if this is not the case, we can yet assume a *mean* diameter  $s_0$ , so that  $m$  becomes  $= \frac{1}{6} \pi s_0^3$ ), we may write:

$$F_0 \sigma^2 = \frac{Nne^2}{s_0} \left(\frac{s_0}{d}\right)^3 \frac{1}{(\frac{1}{6} \pi s_0^3)^2} (\frac{1}{6} \pi s_0^2 \sigma)^2 = \frac{1}{36} \frac{Nne^2}{s_0} \left(\frac{s_0}{d}\right)^3 \frac{1}{b_0^2} (b - b_0)^2 \sigma,$$

in which  $b_0$  is the smallest volume of the molecules. The quantity

<sup>1)</sup> We may point out here, that in consequence of the dimensions of  $e$ , viz.  $\text{gr.}^{1/2} \text{cm.}^{3/2} \text{sec.}^{-1}$  (in electrostatic units),  $F_0 \sigma^2$  properly gets the dimensions of an energy.

$\theta$ , which differs little from 1, has been written by the side of  $(b - b_0)^2$ , because  $\pi s_0^2 \sigma$  represents  $b - b_0$  only when  $\sigma$  is very small. Else we have:

$$b - b_0 = \frac{1}{6} \pi (s_0 + 2\sigma)^3 - \frac{1}{6} \pi s_0^3 = \frac{1}{6} \pi (6s_0^2\sigma + 12s_0\sigma^2 + 8\sigma^3),$$

so that evidently  $\theta$  represents:

$$\theta = [\pi s_0^2 \sigma : \frac{1}{6} \pi (6s_0^2\sigma + 12s_0\sigma^2 + 8\sigma^3)]^2 = (1 + 2\sigma/s_0 + \frac{4}{3}\sigma^2/s_0^2)^{-2} = (1 + \sigma/r_0 + \frac{1}{3}\sigma^2/r_0^2)^{-2},$$

when  $r_0$  represents the smallest radius of the molecule  $= \frac{1}{2} s_0$  (for  $\sigma = 0$ ).

For a substance like Argon, where  $b_k : b_0 = 2\gamma_k = 1,5$ ,  $r_0 + \sigma$  would e. g. be  $= r_0 \sqrt[3]{1,5} = 1,145 r_0$ , hence  $\sigma/r_0 = 0,145$ , and  $\theta = (1,152)^{-2} = 0,75$  (for  $b_k - b_0$ ).

For substances as Fluorbenzene, where  $b_k : b_0 = 1,9$ ,  $\sqrt[3]{1,9}$  becomes  $= 1,239$ , and thus  $\sigma/r_0 = 0,239$ ,  $\theta = (1,258)^{-2} = 0,63$ . For  $H_2$  and  $He$  values will be found nearer 1. Thus for  $He$ , where  $b_k : b_0 = 1,12$ , we get  $\sigma/r_0 = 0,0385$ ,  $\theta = (1,040)^{-2} = 0,92$ . For  $H_2$ , we have  $b_k : b_0 = 1,2$ , so  $\frac{\sigma}{r_0} = 0,063$ ,  $\theta = (1,067)^{-2} = 0,80$ . All these

values refer to the case that (for  $T_k$ ) the atoms (sub-atoms, atomic groups) in the molecule have almost the greatest deviation, as  $b_k$  does not differ much from  $b_g$ . We shall presently have to take this factor  $\theta$  into account.

When we compare the found expression for  $F_0 \sigma^2$  with the term  $A(b - b_0)^2$  in (3), we get for the present:

$$A = \frac{1}{36} \theta \frac{Nne^2}{s_0} \left(\frac{s_0}{d}\right)^8 \frac{1}{b_0^2}, \dots \dots \dots (5)$$

so that the quantity  $A$  in (3), in consequence of the introduction of  $b - b_0$ , through  $\theta$  appears to be dependent on the extent of the deviation in a slight degree — in opposition to the quantity  $F_0$  in (4), in which the original deviation  $\sigma$  occurs. Hence  $A$  is (in a slight degree) both a function of the volume and of the temperature.

Now for infinite volume, according to (3):

$$A_g (b_g - b_0)^2 = fRT,$$

while according to (1):

$$\frac{b_g - (b_0)}{(b_0)} = 0,041 \sqrt{T},$$

in which, as has been said,  $(b_0)$  does *not* represent the real limiting volume  $b_0 = v_0$ , but the limiting volume extrapolated from the direction of the straight diameter at  $T_k$ . We saw in IV, p. 458—459, that e.g. for Argon  $b_0$  is  $= 0,305 v_k$ , whereas  $(b_0) = 0,286 v_k$ . From

$(b_g - (b_0)) : b_0 = 0,041 \sqrt{T}$  follows that for Argon, where  $\sqrt{T_k} = 12,27$ ,  $b_g : (b_0) = 1,503$ . Hence for  $b_g : b_0$  would be found  $1,503 : 1,066 = 1,410$ , because  $b_0 : (b_0) = 0,305 : 0,286 = 1,066$ . Hence the value of  $(b_g - b_0) : b_0$  is  $0,410$ , so that for  $T_k$  this value can be represented by  $(0,410 : 12,27) \sqrt{T_k} = 0,0334 \sqrt{T_k}$ ; and we can, therefore, write — at least for Argon — instead of (1):

$$\frac{b_g - b_0}{b_0} = 0,0334 \sqrt{T} \dots \dots \dots (1^a)$$

From  $A_g (b_g - b_0)^2 = fRT$  and (1<sup>a</sup>) now follows:

$$A_g = \frac{fR}{(0,0334)^2 b_0^2} = 896 \frac{fR}{b_0^2}, \dots \dots \dots (6)$$

in which, as appears from the derivation of (5) from (4), the coefficient 0,0334 will still depend with  $A_g$  on  $T$  through  $\theta_g$  in a slight degree, and is strictly speaking only valid at  $T_k$ , i.e. the temperature at which we calculated just now this coefficient from that of equation (1).

Combination of (5) and (6) now gives immediately:

$$s_0 \left( \frac{d}{s_0} \right)^3 = \frac{1/36 \theta_g \cdot N n e^2}{896 f R} = \theta_g \frac{n^{1/36} \times 6 \cdot 10^{23} \times (4,825 \cdot 10^{-10})^2}{896 \times 83,15 \cdot 10^6}.$$

In this  $(4,825 \cdot 10^{-10})^2 = 23,28 \cdot 10^{-20}$ , and we find:

$$s_0 \left( \frac{d}{s_0} \right)^3 = \theta_g \frac{n}{f} \cdot \frac{3,88 \cdot 10^3}{7,45 \cdot 10^{10}} = \theta_g \frac{n}{f} \times 5,21 \cdot 10^{-8} \dots \dots (7)$$

For  $N$ , AVOGADRO'S value, we have substituted, the most probable one, viz.  $6,0 \cdot 10^{23}$  for  $N$ , as it follows both from PLANCK'S theory of radiation and from the values directly determined by MILLIKAN and NORDLUND. If we namely put for WIEN'S constant of radiation  $c_2 = c (h : k)$  the middle value of WARBURG and COBLENTZ, viz. 1,441, and for STEFAN-BOLTZMANN'S constant  $a$  the mean value of WESTPHAL and several others, viz.  $7,6 \cdot 10^{-15}$ , we find from the wellknown formulae for  $h$  and  $k$ :

$$\beta = h : k = 4,80 \cdot 10^{-11} ; k = 1,393 \cdot 10^{-16} ; h = 6,690 \cdot 10^{-27}.$$

For  $N$  we find therefore  $83,15 \cdot 10^6 : 1,393 \cdot 10^{-16} = 5,97 \cdot 10^{23}$  from  $R = N \times k$ . MILLIKAN'S value is  $6,06 \cdot 10^{23}$ ; NORDLUND'S is  $N = 5,91 \cdot 10^{23}$  (Z. f. Ph. Ch. **87**, p. 62). The mean of these three values is  $5,98 \cdot 10^{23}$ , so that with some probability we may assume about  $6,0 \cdot 10^{23}$  for  $N$ .

For  $N \times e$  has been found  $107,88 : 0,001180 = 96494$  Coulomb = = 9649,4 electromagnetic units =  $2,895 \cdot 10^{14}$  electrostatic units. Hence we find for the value of the electric elementary quantum  $e$  after division by  $N$  the value  $4,825 \cdot 10^{-10}$ .

3. We may now proceed to compare the value of  $s_0$ , found in (7), with the values of  $s_0$  calculated by other methods.

If we put  $n=1$ ,  $f=1$ , so monovalent atoms or atom groups, resp. subatoms, and three degrees of freedom<sup>1)</sup> corresponding to the spacial conception of the molecular vibrators, then:

$$s_0 \left( \frac{d}{s_0} \right)^3 = \theta_g \times 5,21 \cdot 10^{-8},$$

in which  $\theta_g$  represents the value of  $\theta$  at the greatest deviation  $d$  corresponding to  $b_g$  (accurate at  $T'_k$ ). And because we have calculated above the coefficient 0,0334 in (1<sup>a</sup>) from data concerning Argon, we shall also now substitute the value, which we have found for Argon, viz. 0,75 (also at  $T'_k$ ) for  $\theta_g$ . Hence

$$s_0 \left( \frac{d}{s_0} \right)^3 = \pm 3,9 \cdot 10^{-8} \text{ c.M.}, \quad . \quad . \quad . \quad . \quad (7a)$$

in which the found value 3,9 will hold by approximation for all substances on account of the generality of our considerations — at least for substances with not too complex molecules, where also the values of  $s_0$  appear to differ only little.

Let us now calculate the values for  $s_0$  for Argon, Hydrogen, and Helium. The values given before for them are most of them inaccurate, partly in consequence of the value of  $N$ , which was assumed too high (viz.  $6,82 \cdot 10^{23}$  according to PERRIN, instead of  $6,0 \cdot 10^{23}$ ), partly in consequence of inaccurate suppositions on  $b$  (e.g.  $b=4m$ ), or formulae which do not hold without reservation, as e.g. that of the mean length of way, from which then  $s_0$  was calculated (viz.  $\pi N s_0^2 = v : l \sqrt{2}$ ).

For Argon a liquid density = 1,374 is found at  $-183^\circ$ . From this follows for the molecular volume  $(39,88 : 1,374) : 6 \cdot 10^{23} = 48,4 \cdot 10^{-24}$ . As the molecules have not yet approached each other in this state to the shortest distance, we must assume that  $s_0$  is smaller than the longitudinal dimension of the cubes, the volume of which amounts to the above value. Hence we have  $s_0 < 3,64 \cdot 10^{-8}$ .

We can also calculate  $s_0$  from  $\beta_0 = b_0 : v_k = 0,305$ . As  $v_k = 39,88 : 0,5308 = 75,13$ , we get  $b_0 = 0,305 \times 75,13 = 22,92$ . The molecular

<sup>1)</sup> In (3)  $f$  was namely the factor of  $RT$ . Of course our considerations are only valid for not too low temperatures, as otherwise the limiting term  $RT$  must be replaced by the known more intricate form on account of the quanta effect. As, however, the *intra*-molecular vibrations will probably have a greater frequency than those of the molecules themselves, the temperature at which the influence of the effect in question will already make itself felt, will in general be higher than the corresponding temperature for the molecular system.

volume is therefore  $38,2 \cdot 10^{-24}$ . If in this shortest distance we still assume approximate cubic distribution<sup>1)</sup> of the molecules, then  $s_0$  becomes  $\geq 3,37 \cdot 10^{-8}$ , which agrees very well with the just calculated upper limit<sup>2)</sup>.

We may therefore assume for argon  $s_0 = 3,5 \cdot 10^{-8}$  cm.

PERRIN gives for this (Conseil Solvay, German edition, p. 154), the somewhat too low value  $2,7 \cdot 10^{-8}$ , calculated from the length of path.

For *Hydrogen* we find 0,086 (DEWAR) for the density at the melting point<sup>3)</sup>. Hence  $s_0^3 < (2,0152 : 0,086) : 6 \cdot 10^{23}$ , or  $s_0^3 < 39,1 \cdot 10^{-24}$ ,  $s_0 < 3,39 \cdot 10^{-8}$ .

The value of  $b_0$  at  $H_2$  being only known by approximation, no lower limit can be given. The value of  $b_0$  calculated by me before (These Proc. of April 24, 1903) by means of VAN DER WAALS' equation of state of the molecule is not suitable for this purpose. I found then namely  $b_g$  almost independent of the temperature, on the other hand  $b_0$  increasing with  $T$ , which is not probable. If for  $b_g$  the value 0,000917, found before, is assumed, we find about 0,00076 for  $b_0$  with  $b_g : b_0 = 1,2$ , hence  $s_0^3 \geq (0,00076 \times 22412) : 6 \cdot 10^{23} \geq 28,3 \cdot 10^{-24}$ , or  $s_0 \geq 3,05 \cdot 10^{-8}$ .

[We once more draw attention to this, that if we had put  $b = 4m$  according to the current assumption, and  $b_0 = \pm 2m$  according to the theory of the apparent diminution of  $b$ , we had found a much too small value for the lower limit].

For the present we can therefore assume  $s_0 = \pm 3,2 \cdot 10^{-8}$  for  $H_2$ .

The value  $4 \cdot 10^{-8}$ , calculated from unknown data, which I found given somewhere, is therefore slightly too great.

1) I. e. that even at the greatest density the molecules do not occupy a smaller volume than  $s_0^3$ . Only on the supposition of perfect spherical form, and the entire lack of impenetrable spheres of influence (see § 1) could it be assumed that a smaller minimum volume than  $s_0^3$  were possible. This, however, seems a physical impossibility to me, and — like the assumption of an apparent diminution of  $b$  in consequence of the partial overlapping of the distance spheres — only a mathematical fiction. Also the existence of crystal nets seems to plead strongly against the assumption of a denser accumulation than corresponds with  $s_0^3$ . It might sooner lead us to the opposite conclusion.

2) The sign of inequality  $>$  namely refers to the *possibility* that the molecules can occupy a somewhat smaller volume than  $s_0^3$ .

3) To my regret I have no tabular works as the latest edition of LANDOLT UND BÖRNSTEIN, *Recueil de constantes physiques*, and others at my disposal, so that I had to be content with this slightly antiquated value of DEWAR. I do not know any clear summary of the constants determined in the Leiden Laboratory for different substances. Neither in KAMERLINGH ONNES and KEESOM's book on the equation of state, nor in that of KUENEN did I find, except incidentally, numerical values of experimentally determined constants.

For *Helium* KAMERLINGH ONNES (Suppl. 21) has found  $d = 0,15$  for liquid *He*. Hence  $s_0^3 < (3,99 : 0,15) : 6 \cdot 10^{23}$ , or  $s_0^3 < 44,5 \cdot 10^{-24}$ , therefore  $s_0 < 3,54 \cdot 10^{-8}$ .

If for  $b$  in the case of *He* the value 0,0007, given in Suppl. 21, is assumed, then  $b_0$  is about  $0,007 : 1,12 = 0,000625$ , hence  $s_0 \geq (0,000625 \times 22412) : 6 \cdot 10^{23}$ , i.e.  $\geq 23,35 \cdot 10^{-24}$ , or  $s_0 \geq 2,86 \cdot 10^{-8}$ .

This value is evidently too small; perhaps the  $b$ -value, for which K. O. first (Comm. 102a) gave 0,00043, and which was later on raised to 0,0007, must be raised somewhat more.

We therefore assume for *He* the middle value  $s_0 = \pm 3,2 \cdot 10^{-8}$ .

PERRIN's value, viz.  $1,7 \cdot 10^{-8}$  (loc. cit.), is at any rate too low.

It appears from the above examples, that for three substances which differ so much as Argon (mol. weight = 40), Helium (mol. weight = 4) and the di-atomic  $H_2$  (mol. weight 2), the values of  $s_0$  differ very little.

Also on calculation of other not too complex substances  $s_0$  appears to rise very rarely above  $4 \cdot 10^{-8}$ .

The found values are in better harmony than could be expected with the value  $\pm 3,9 \cdot 10^{-8}$ , which follows from our theoretical considerations. Not only is the order of magnitude the same, but even the numerical value is almost identical.

When we bear in mind that  $s_0 \cdot (d : s_0)^3 = 3,9 \cdot 10^{-8}$ , then  $(d : s_0)^3 = 1,11$  would follow from e.g.  $s_0 = 3,5 \cdot 10^{-8}$  (for Argon), hence  $d : s_0 = 1,04$ . The diameter of the molecule would therefore be a little smaller than the distance of equilibrium  $d$  of the two charges, which might point to a somewhat elongated form of the molecule, because then the mean diameter  $s_0$  would be somewhat smaller than the distance of the centres, in which the charges may be imagined fictitiously concentrated. But though this supposition is very plausible, particularly for di-atomic gases, yet there is by no means certainty on this head on account of the not absolute accuracy of the calculated values. The more so as there may also be other influences at work, of which we only mention that of the degrees of freedom by which the factor  $f$  is influenced; and also the influence of the deviation from the law of equipartition, through which in (3) the factor  $f$  would apparently become smaller. But even when we leave the factor  $(d : s_0)^3$  in (7a) out of account, the concordance between the value of  $s_0$ , calculated from the assumption of electrical forces and the values found for different substances, in connection with VAN DER WAALS' equation of state of the molecule and the temperature coefficient of  $(b_g - b_0) : b_0$  found by me, remains remarkably close.

*Fontanivent sur Clarens, October 1914.*

**Physiology.** — "*Exaggeration of Deep Reflexes.*" By Prof. J. K. A. WERTHEIM SALOMONSON.

(Communicated in the meeting of November 28, 1914).

The graphic method of recording pathologically exaggerated deep reflexes sometimes offers interesting results.

In the literature we find mentioned that exaggeration may show itself in different ways. A very slight tap on the tendon produces an unusually brisk contraction: the threshold-value of the stimulus is lowered. But we also read that the latency is shortened, that the duration, velocity and height of the contraction are increased; that a simple jerk may be changed into a tonic or clonic contraction. But even with this knowledge we are not quite prepared for the multiformity of the curves which may be recorded.

I have tried to record the shortening, or more generally the thickening of a muscle, following a tap on its tendon. Of course I found more or less of the changes mentioned before. But the curves seemed to be so absolutely different that I could not be content with the simple statement, that some patients showed one form of curve, some other patients quite another curve. We should like to know at least something about the mechanism of these different forms.

A priori the idea of a change in the form caused simply by exaggeration of a reflex is rather difficult to conceive. We can readily understand that the reflex irritability is increased when an extremely slight tap on the tendon produces a very strong contraction. And this is conformed by clinical examination. But it is now generally understood, — and I think I too have contributed to this opinion — that the deep reflexes must be considered from a physiological point of view as simple contractions, preceded by one double-phased current of action. As physiological variations in simple muscle-twitches we only know slight changes in height, duration and slope of the curves, caused by fatigue, by temperature etc., if we abstract from the changes caused by direct poisoning. But we do not know of an increased shortening, of a notable change in the latency or of a highly increased duration as long as we consider only simple muscle-twitches.

If the simple muscle-twitch of the quadriceps known as knee jerk be recorded, we find under physiological conditions that the duration of the twitch is very nearly 0.20 second.

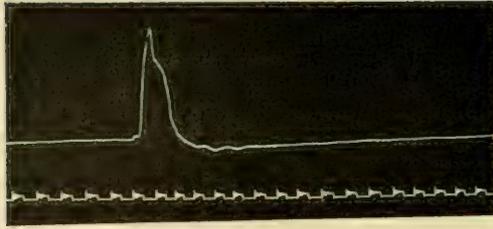


Fig. 1.

In many cases of undoubted exaggeration of the knee-jerk we also find very nearly 0.20 second. Fig. 1 shows such a curve in which the time marks, as in all the other curves in this paper represent 0.1 second. This record must be considered as an instance of the simplest form of an exaggerated deep reflex. I can add that this simplest form is rather a rare one and that more complicated forms are more usually met with. All the more complicated forms are characterised by the occurrence of more than one top in the graphical record. Amongst these we must consider in the first place the *simple clonic reflex*, where the simple twitch is entirely absent and replaced by a small series of clonic contractions (fig. 2). These

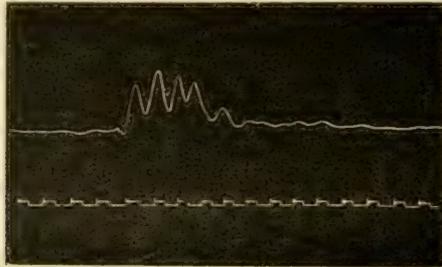


Fig 2.

are generally rather limited in number and we find perhaps only 4—7 contractions in all. But in a few cases quite a long series of clonic contractions may be seen (fig. 3). Curves of this kind may be found in patients where the mechanical and physiological conditions for permanent clonus are present. This means that the reflex irritability as well as the muscle tonus are greatly increased; also that the leg of the patient must be kept in such a position that nothing prevents the occurrence of clonus. Clinically we can find this in patients with organic as well as functional diseases of the nervous system. In functional disorders even the tonic rigidity of the muscles need not be present as a state of active muscle contraction may provide the mechanical condition for a clonus as well as a tonic spasm does.

But under such conditions the clonus generally is not quite as regular as in organic disorders, as is well known. The very short cloni, as in fig. 2, were only seen in organic diseases of the central nervous system.

The complicated forms of deep reflexes, which are now to be considered, offer the peculiarity that after an initial simple twitch, the muscle does not entirely relax, but a state of hardening of the muscle substance persists for a longer or shorter time. This hardening may be caused in at least three different ways.

Fig. 4 represents a record obtained in a patient with chorea minor and shows one of the changes described by GORDON, HEY *a. o.* as occurring in chorea minor. After the initial simple twitch we observe a second contraction which may be as high or even higher than the first. It begins either at the end of the simple twitch or even a little earlier. In this special case the second contraction showed the short duration of a single twitch, but I have also seen more tonic contractions in the same patient as well as in others with the same disease. The latency of this second contraction is of the order of 0.15—0.20 second and agrees with the latency for a central reaction on a stimulus applied to the peripheral organs of sense. As the probable seat of the lesions in chorea is the cerebrum, we must at least consider the possibility of a central reaction. It seems to me that this supposition is not entirely unfounded. I even think it rather probable, that the deep reflexes are also, at least partially represented at a higher nervous level than the spinal cord. In peculiar circumstances, as in chorea minor, this cerebral part may sometimes appear. I think that this cerebral part of the reflex is answerable too for the so-called pseudo-kneejerk of WESTFAHL, which in rare cases of tabes appears with a latency of about 0.2 second after tapping the knee-tendon or the skin above it. In more than a few cases of functional neurosis I have also seen reflexes as in fig. 4. I have never been able to record those reflexes, which as a matter of fact occurred only the first time that the knee-jerk was elicited; if the reflex was obtained a second time or at a later examination, the cerebral restraining impulse was sufficiently intense to prevent the action of the higher centrum. In chorea this restraining influence has entirely disappeared as well as the faculty of suppressing involuntary choreatic movements.

Records closely resembling those of fig. 4 can be obtained sometimes under totally different circumstances. Fig. 5 was recorded in a case of multiple sclerosis, the patient being nearly paralysed. He is just able to make a few slow movements with his extremely rigid

lower limbs. The kneejerk shows a simple twitch followed by a second and even a third short contraction; immediately afterwards a second kneejerk showed a contraction of half a second's duration following the initial twitch.

In cases like this we scarcely need consider a central origin for the

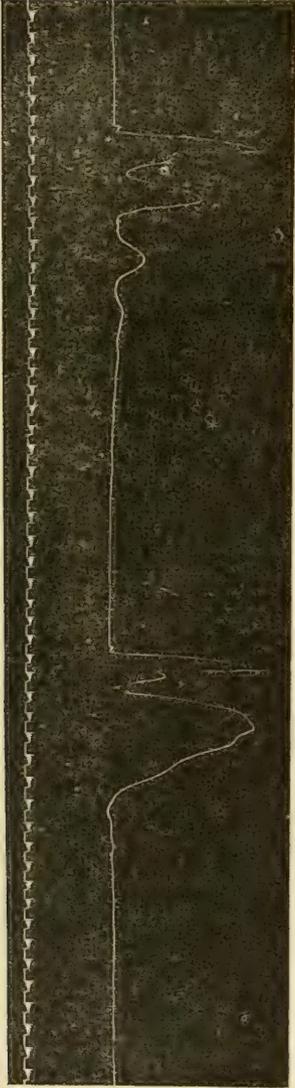


Fig. 5.

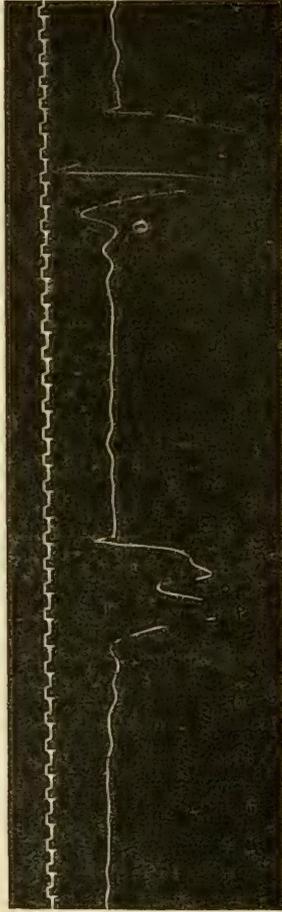


Fig. 4.

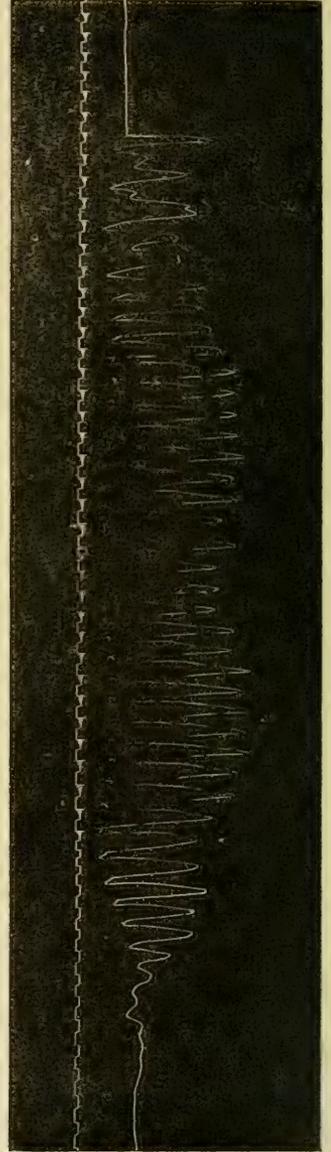


Fig. 3.

second contraction especially as contractions of this kind are sometimes found in completely paralysed patients. In some cases of myelitis or tumor of the spinal cord with complete paralysis we may often see involuntary movements in the paralysed limb. These movements set in after a slight peripheral stimulus, such as a simple touch, or the influence of the lower temperature of the air, or even without appreciable cause; they cannot be prevented or modified by the patient. They may be considered as a spinal automatism. Generally they appear in the form of an adduction or a flexion of the lower limbs, more rarely as an extension movement. But a tap in the neighbourhood of the knee often produces a stretching movement of the leg.

In some records it is not easy to distinguish between a clonus *strictiori sensu* and an automatism. The oscillations in the curve of

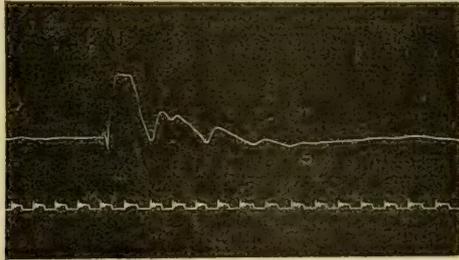


Fig. 6.

fig. 6 are rather slow for a true clonus, the rhythm being not quite 5 per second. For an automatism the rhythm is rather fast. Perhaps we might consider it as an intermediate form: clonus and automatism are sufficiently closely related to render this admissible.

There is still a third possible genesis for the after-contraction. In a former communication on "shortening reflexes" I pointed out, that these are always accompanied by a tonus-reflex, by which the muscle adapts itself to its new condition. As soon as a movement is necessary the muscle tonus is automatically regulated so as to put the muscle in the best condition for doing its work. Therefore we may a priori expect a tonus-reflex at the same time as the deep reflex. As a matter of fact we find that in records of simple deep reflexes, the simple twitch is generally followed by a slight elevation of the curve, indicating that immediately after the real muscle twitch tonus is increased for somewhat less than a second. The beginning of the tonus reflex is not sharply defined, as it starts before the end of the simple twitch. In favourable circumstances this after-contraction

shows a smooth curve; more often we find a clonical after-contraction (fig. 7). Records of this kind are obtained in cases where

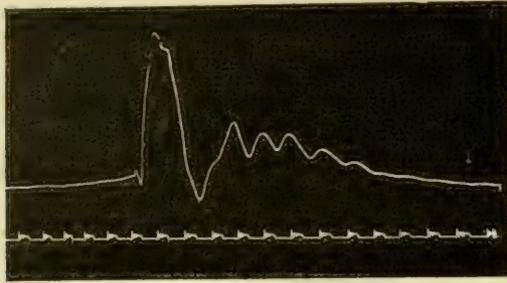


Fig. 7.

in ordinary conditions the tonus is not quite high enough to permit of a clonus. But as soon as a tap on the tendon elicits the muscle twitch and the tonus reflex, the tonus sufficiently increases to render a short clonus possible. This last disappears as soon as the tonus reflex is finished. If we can in some way diminish the tonus before the reflex is obtained, the increase of tonus caused by the reflex may be insufficient for a clonus. In such a case we should be able to provoke either a tonic or a clonic after-contraction, only by lowering or increasing the tonus beforehand. Resting the foot, slight active bending of the knee diminishes the tonus in the quadriceps; supporting the knee and slight passive bending increases it.

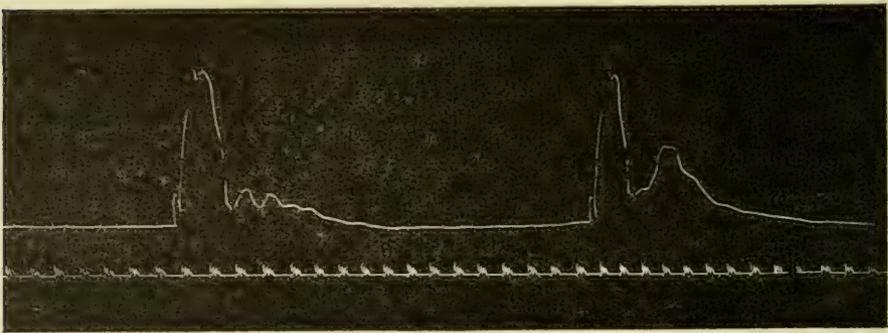


Fig. 8.

Fig. 8 gives a record on which the first reflex shows a clonic, the second one a tonic aftercontraction, which were obtained in this way. With all patients of this kind the tonus is not quite sufficient to admit of a persisting clonus. Only under the most favourable circumstances, as after prolonged exposure to a low temperature, and much care in arranging the most favourable

positions of the lower limbs, we may be able to produce a damped clonus or perhaps even a permanent clonus.

We have now to consider another group of records in which the after-contraction forms the most important and conspicuous part in the whole reflex.

Fig. 9 gives an exceedingly protracted after-contraction of nearly 5 second's duration. Clinical observation shows that this is not a case of spinal automatism. In testing the knee-jerk we find that the leg is extended in the ordinary way, or perhaps a trifle longer, and falls down as in a normal reflex. But we see and feel, that the tendon remains in a state of maximal tension and that the muscle itself retains its condition of increased tonus. Then the tonus disappears slowly and gradually and only after several seconds the original condition has returned. That we have indeed a tonus variation of excessive magnitude before us and not a contraction *strictiori sensu*, may be seen from fig. 10. This record was obtained from the same patient suffering from *diplegia cerebialis pseudobulbaris* and shows two knee-jerks in succession, the second being elicited before the first had entirely subsided. The second jerk shows, in exactly the same way as the first a maximal simple twitch, whereas afterwards the tonus was still more exaggerated. As the second jerk gives a record which in this patient must be regarded as a customary one, a real contraction ought to be considered as highly improbable. Neither is the hypothesis of an automatism very alluring, as this patient did not show any other typical spinal automatic movement. Finally the clinical examination showed, that in the almost paralysed patient all changes of the muscle tonus disappeared very slowly, and agreed absolutely with the after-contractions of the knee-jerk.

In another patient with *diplegia cerebialis* the knee-jerk produced quite a series of interesting movements, as will be seen in the records of fig. 11—13. In fig. 11 we find that the initial twitch can be followed by a protracted tonic aftercontraction, on which either clonic movements with a rhythm of 8 per second are superposed or not. In other circumstances, principally determined by the position of the limb, and the way of supporting it during the examination, I could get a series of automatic movements with a rhythm of about  $2\frac{2}{3}$  per second. At the same time the clonus of 8 per second remained more or less visible (fig. 12). By a slight change in the way of supporting the knee it was possible to obtain much longer duration of the automatic movements (fig. 13); the more rapid clonus disappeared completely after a few seconds

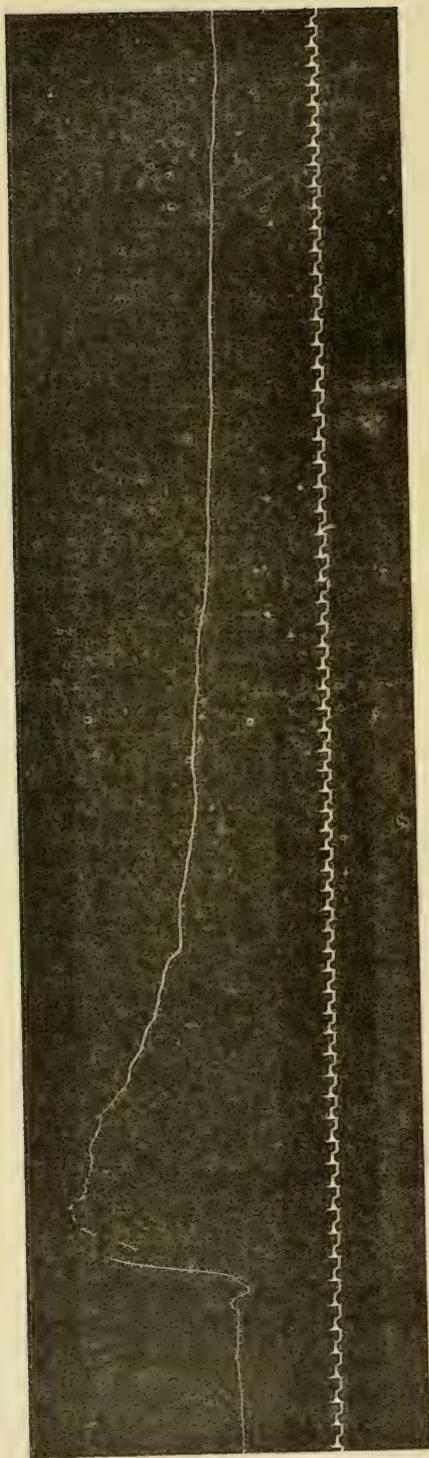


Fig. 9.

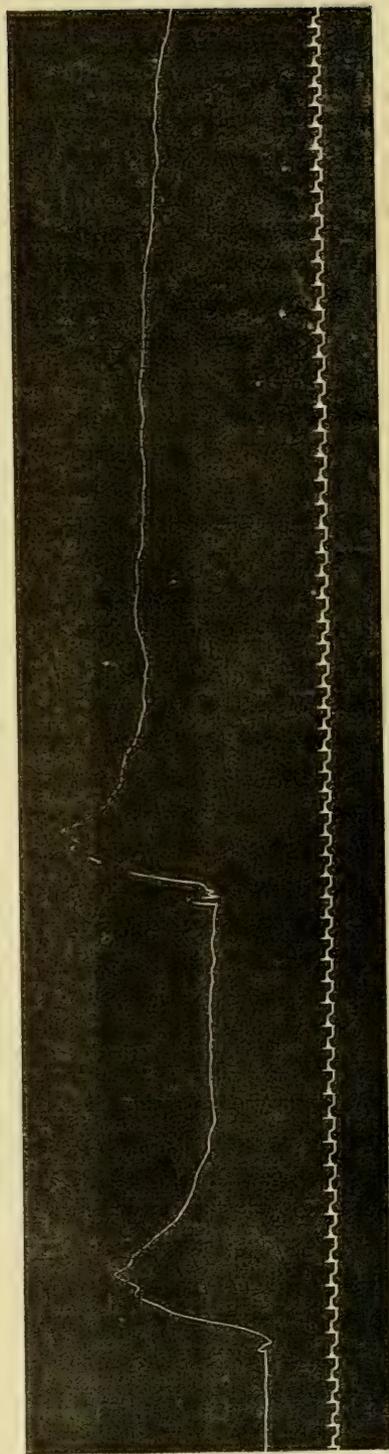


Fig. 10.

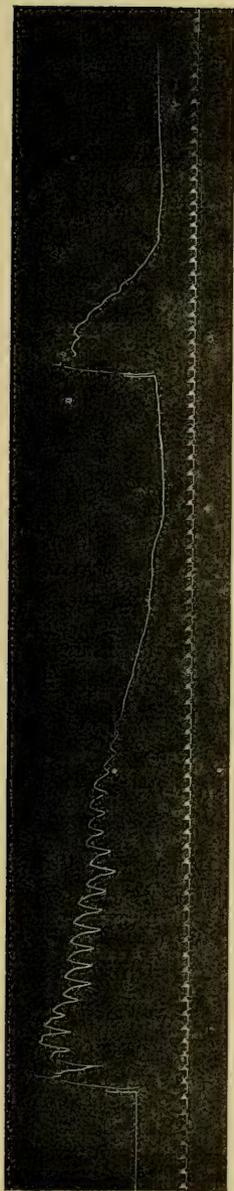


Fig. 11.

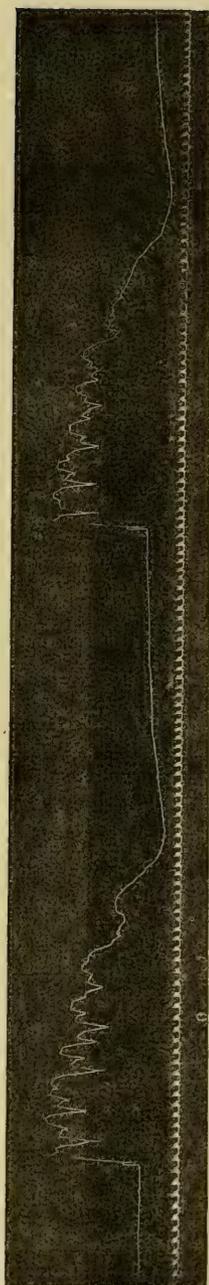


Fig. 12.



Fig. 13.

and only the slow automatic extension and flexion movement with a rhythm of  $2\frac{2}{3}$  per second remained visible, often during 30 seconds and longer.

All the records shown in this paper are obtained from the patellar tendon-reflex. Yet their significance is more general, as also other exaggerated deep reflexes sometimes show changes of a similar nature.

**Physics.** — “*The specific heat at low temperatures. I. Measurements on the specific heat of lead between 14° and 80° K. and of copper between 15° and 22° K.*” By W. H. KEESOM and H. KAMERLINGH ONNES. Communication N°. 143 from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of October 31, 1914).

§ 1. *Introduction.* Soon after the methods of obtaining baths of temperatures which are accurately known and can be kept constant for a long time, in the range between the boiling point and the melting point of hydrogen, had been worked out<sup>1)</sup> in the cryogenic laboratory at Leiden, a series of investigations on the calorimetry at very low temperatures was started there. DEWAR's measurements on the mean specific heat of different substances between the temperature of liquid air and the boiling-point of hydrogen<sup>2)</sup> had particularly drawn attention to the interest of those investigations. The continuation of his experiments in the still lower region of temperatures mentioned above seemed very desirable<sup>3)</sup>. As was done by DEWAR the series of investigations in this direction was begun by determinations of the heat of vaporisation of hydrogen. A report on the first results of those determinations was given at the Dutch

<sup>1)</sup> Cf. specially H. KAMERLINGH ONNES, Leiden Comm. N°. 94*f* (Proceedings Sept. '06) and H. KAMERLINGH ONNES, C. BRAAK and J. CLAY, Leiden Comm. N°. 101*a* (Proceedings Dec. '07).

<sup>2)</sup> J. DEWAR, Proc. Roy. Inst. March 25, 1904, Proc. Roy. Soc. A 76 (1905) p. 325, later more extensively between the boiling point of nitrogen and that of hydrogen: Proc. Roy. Soc. A. 89. (1913) p. 158.

<sup>3)</sup> This was pointed out at the 1st International Congress of Refrigeration at Paris 1908. H. KAMERLINGH ONNES, La liquéfaction etc. Note J. Sur les expériences à faire aux températures très basses. Leiden Comm. Suppl. N°. 21*a* p. 29.

Congress of Science and Medicine at Groningen (1911)<sup>1)</sup>. An investigation regarding the specific heat of lead, after which other metals were to follow, at hydrogen temperatures, an investigation which had a particular interest with a view to EINSTEIN'S theory and also in connection with <sup>2)</sup> NERNST'S theorem, was announced on that occasion.

Since then in NERNST'S laboratory a highly important series of investigations on the specific heat has been made by himself and by his collaborators <sup>3)</sup>. In particular the investigations on solids at low temperatures, which had already been made down to the temperatures of liquid air boiling under reduced pressure, were continued to the temperatures which can be obtained with liquid hydrogen. Besides KAMERLINGH ONNES and HOLST <sup>4)</sup> made preliminary measurements of the specific heat of mercury at helium temperatures. The investigations mentioned have already furnished a great number of highly valuable data, which in particular have served for a test of the theories of DEBIJE <sup>5)</sup> and of BORN and v. KÁRMÁN <sup>6)</sup>. The method we followed is mainly that which has been developed by NERNST and EUCKEN. Notwithstanding all that the continuation of our programme seemed to remain desirable. First, when NERNST'S investigations had followed the specific heat down to the region of hydrogen temperatures, because only a few of his observations entered into this region and the accuracy of the observations left some doubt with NERNST himself, and later, when between the boiling point and the melting point of hydrogen also more accurate determinations had been made in his laboratory <sup>7)</sup>, because for the investigation of the questions which

1) W. H. KEESOM. The heat of vaporisation of hydrogen. *Handel. 13de Ned. Nat. en Geneesk. Congres*, April 1911, p. 181. Published also *Leiden Comm. N<sup>o</sup>. 137e*.

2) Cf. also H. KAMERLINGH ONNES. Reports of the II<sup>nd</sup> International Congress of Refrigeration. Vienna 1910 (*Comm. Leiden Suppl. N<sup>o</sup>. 21b* p. 42).

3) For the literature we refer to *Leiden Comm. Suppl. N<sup>o</sup>. 23* "Die Zustands-gleichung" *Math. Encycl. V.* 10 Note 838. Later: A. EUCKEN and F. SCHWERS. *Verh. d. D. phys. Ges.* 15 (1913) p. 578, W. NERNST and F. SCHWERS. *Berlin Akad. Sitz. Ber.* 1914 p. 355. R. EWALD *Ann. d. Phys.* (4) 44 (1914) p. 1213.

4) H. KAMERLINGH ONNES and G. HOLST. *Comm. N<sup>o</sup>. 142c* (Sept. '14).

5) P. DEBIJE. *Ann. d. Phys.* (4) 39 (1912), p. 789. W. NERNST and F. A. LINDEMANN *Berlin Akad. Sitz. Ber.* 1912, p. 1160. Cf. also W. NERNST, *Vorträge Wolfskehl Congress Göttingen 1913*, p. 61.

6) M. BORN and TH. v. KÁRMÁN. *Physik. ZS.* 13 (1912), p. 297; 14 (1913), p. 15, 65. H. THIRRING, *Physik. ZS.* 14 (1913), p. 867; 15 (1914), p. 127, 180. Cf. M. BORN, *Ann. d. Phys.* (4) 44 (1914), p. 605.

7) A part of our observations had already been made when the results of EUCKEN and SCHWERS were published (see § 5). The completion of even the limited part of the programme, which is contained in this communication, has been much retarded, partly by the wish to attain very trustworthy results.

have now come to the front a high degree of accuracy is desirable.

In this respect it was an advantage: 1<sup>st</sup> that particularly by the investigation of KAMERLINGH ONNES and HOLST<sup>1)</sup> on the scales of the hydrogen and the helium constant volume thermometers we could avail ourselves of a more accurate temperature scale<sup>2)</sup>; 2<sup>nd</sup> that the cryostats used at Leiden allowed the measurements to be performed under more favourable circumstances in other respects also. In fact in the measurements published in this paper an accuracy of 2% has been reached at hydrogen temperatures, while there is reason to expect that in subsequent measurements the accuracy will still be considerably increased.

§ 2. *Method. Apparatus.* We followed with some modifications the method which has been in particular developed by NERNST and EUCKEN, and which has shown itself to be very suitable for low temperatures. In this method a block of the metal to be investigated, provided with wires for heating and temperature measurement, is suspended in a vacuum which is made as perfect as possible. Within the block a measured quantity of heat is developed by an electric current, and the increase of temperature produced is measured.

Fig. 1 represents the cryostat with the calorimeter. To protect the block against the residual heat radiation which enters the calorimeter vessel  $C$  (the vacuum-vessels are silvered a slit being left open), it is silvered on the outside up to a few mms. below the sealing-places  $C_2$  of the platinum wires. Moreover the plate  $C_1$ , which through a platinum wire is in heat conducting connection with the bath, prevents radiation from above.

In the block  $B$  of the metal to be investigated a chamber has been drilled, into which the core  $K$  fits tightly. This core contains the wires which serve for heating and for measuring the temperature; when the temperature wire has once been calibrated and the heat capacity of the core measured separately, it can serve for the successive measurements of the specific heat of all the metals of which suitable blocks can be made, and of other substances also when use is made of a suitable vessel. The core consists (Fig. 2) of a solid cylinder  $K_1$  and two cylindrical mantles  $K_2$  and  $K_3$ , all

<sup>1)</sup> H. KAMERLINGH ONNES and G. HOLST. Comm. No. 141a (May 1914).

<sup>2)</sup> The temperature scale used by NERNST, and also those of EUCKEN and SCHWERS and of NERNST and SCHWERS are mainly based upon the older calibration of the thermometer *Pt1* by KAMERLINGH ONNES, BRAAK and CLAY, which has to be replaced by the newer one of KAMERLINGH ONNES and HOLST. Cf. further § 3.

of copper, provided above with flat, tightly fitting collars, and of a copper plate  $K_4$ , which is in addition connected with  $K_1$  by means

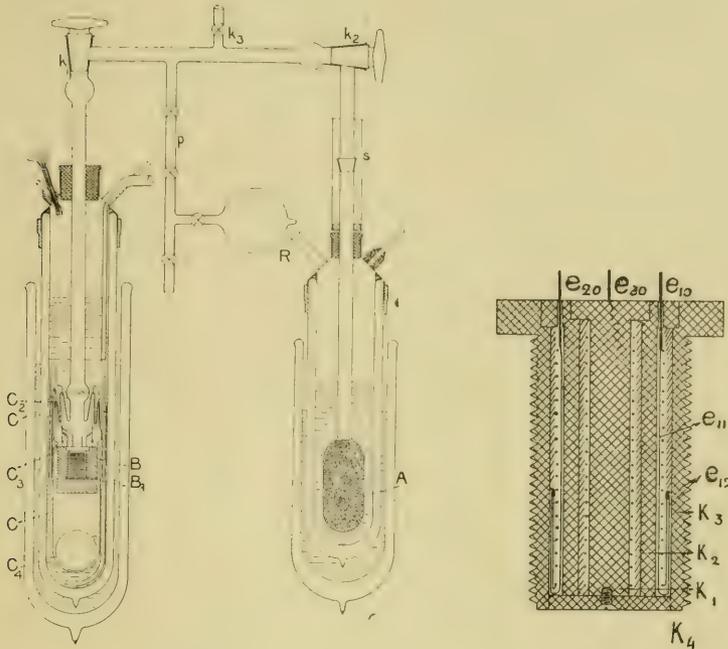


Fig. 1.

Fig. 2.

of a copper screw. Round  $K_1$  a gold wire has been wound doubled on itself; for insulation and at the same time for heat conduction enamel and thin paper were used; the electrodes  $e_{10}, \dots, e_{40}$ , stout platinum wires (1,5 mm.), which are led through the collars and insulated from these, and protrude outside the core, are rolled out below to flat bands which are a few centimeters longer than the cylinder; to the ends of these the gold wire is soldered with gold, after which the band was bent up ( $e_{12} \dots$ ) and fastened to the core and insulated.

The space which remained within  $K_2$  was filled up with the copper-tin-amalgam which is used in dentistry. In the same way a constantin wire was wound round  $K_2$  and enclosed between  $K_2$  and  $K_3$ . Then the whole was closed by the plate  $K_4$  below, and the different parts were united as much as possible by Wood-metal. The insulation was tested with an insulation meter and found to be more than sufficient.

The block  $B$  is suspended from two platinum wires (0.6 mm.) with the aid of two small glass rings. These platinum wires serve at the same time for conduction of the heating current. They are therefore connected to the electrodes of the constantin wires by platinum wires (0,2 mm.). For simplicity the wires, which serve for measuring

the potential difference between the electrodes  $e_{10}$ ,  $e_{20}$  of the constantin wire, are applied outside the calorimeter vessel near the sealing places. The resistance between these junctions and the ends of the constantin wire is inappreciable compared with the resistance of the latter (140  $\Omega$ ). For the gold wire, which serves as a thermometer, potential as well as current wires (within the calorimeter vessel 0.1 mm. platinum; insulated with silk) lead directly to the electrodes.

The stopcocks  $k_1$  and  $k_2$  have wide borings,  $k_3$  leads to a GAEDE mercury pump, which serves for evacuating the charcoal and for a preliminary evacuation of the calorimeter vessel, and to a Mc.-Leod gauge,  $R$  is a reservoir which is filled with hydrogen; with the aid of the pipette  $p$  a quantity of this hydrogen is admitted into the calorimeter vessel when it is required to bring about heat conduction between the block and the bath.

The charcoal tube  $A$ , made of glazed opaque quartz, was filled with cocoa-nut charcoal, and evacuated for a sufficient time at 600° C. before each series of measurements. During the measurements it is cooled with liquid hydrogen.

To diminish the exchange of heat between the metal block and the bath through the conducting wires, during the measurements the bath that surrounds the calorimeter was brought as nearly as possible to the temperature at which the measurement was to be made. The time-rate of the temperature before the heating and after the heating, at least after a few tens of seconds, was as a rule very small, if not inappreciable. For illustration in Fig. 3 and 4

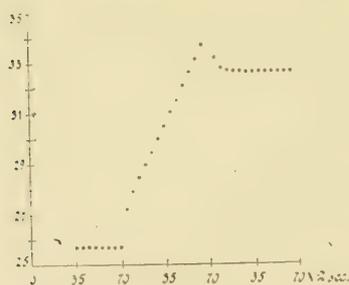


Fig. 3.

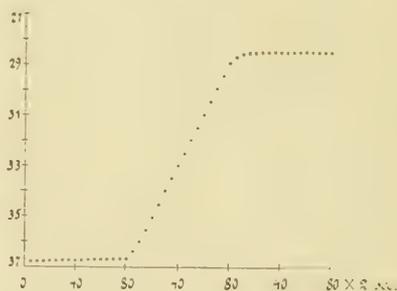


Fig. 4.

the time-curve of the galvanometer, which indicates the temperature, during two measurements is represented, viz. for a measurement of the specific heat of lead (Fig. 3) and for a measurement of the specific heat of copper (Fig. 4), respectively. The increase of temperature was in both cases about 1 degree. In the measurement with

lead the temperature of the core appears to have risen about  $\frac{1}{6}$  degree above the mean temperature of the lead block during the heating, in the measurement with copper, for which the heat supply per second was chosen smaller in accordance with the smaller specific heat, the corresponding temperature difference is not appreciable. Where necessary, corrections for the heat exchange with the bath were applied.

*The heat supply.* The arrangement for sending a current of measured intensity and potential difference during a definite time through the constant heating wire is represented in Fig. 5 together with the arrangement <sup>1)</sup> for measuring the resistance of the gold thermo-

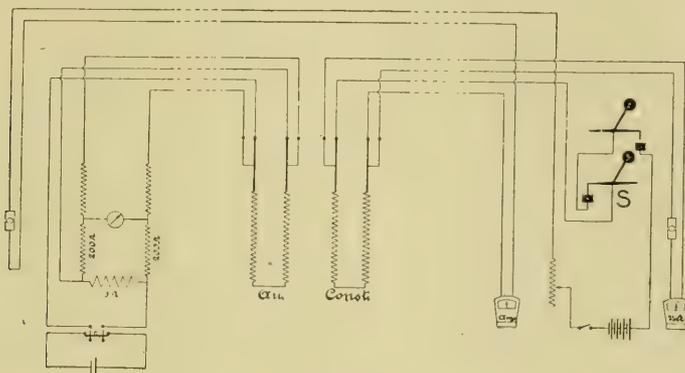


Fig. 5.

meter wire. Intensity and potential difference were read on accurate WESTON millivolt- and voltmeters. These were calibrated repeatedly for the measuring ranges used with the aid of a standard element of the WESTON Cy., standard resistances and a compensation apparatus free from thermoelectric forces with an auxiliary apparatus according to DIESELHORST, all calibrated at the Physikalisch Technische Reichs-

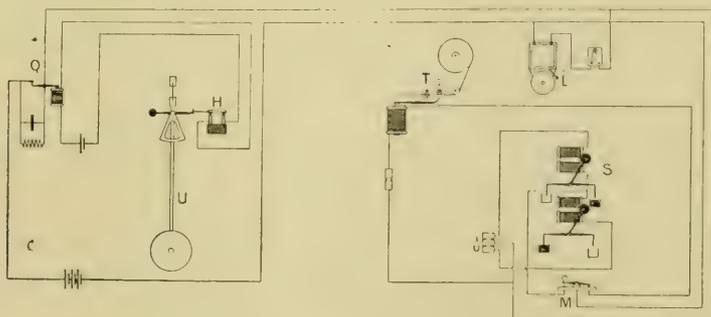


Fig. 6.

<sup>1)</sup> In the figure the regulating resistance and the milli-ampèremeter between accumulator and commutator have been omitted.

anstalt. The switch  $S$  for closing and opening the current served for measuring off the time. Fig. 6 represents the complete arrangement<sup>1)</sup> for measuring off and registering the time. The clock  $U$  with second pendulum, provided with a Hönw's registering arrangement  $H$ ,

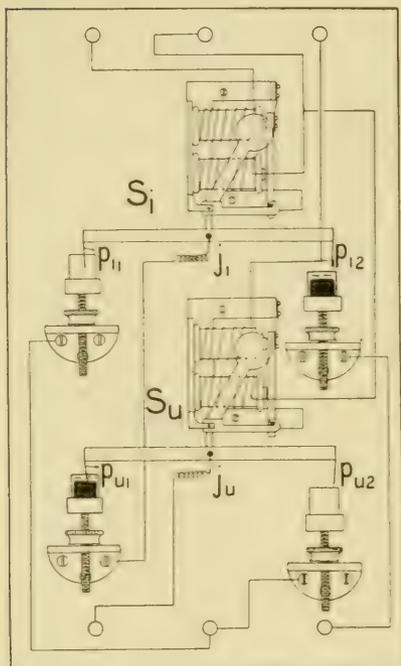


Fig. 7.

the contact plug having been transferred from  $i$  to  $u$ . As a control the moments of switching in and out are registered by  $T$  (Fig. 6) through the corresponding dash on the paper strip being absent.

An accuracy of  $1/10$  of a second is certainly attained with this arrangement.

*The temperature measurement.* The scale of the gold resistance thermometer is dealt with in § 3. In Fig. 6 the Thomson bridge

<sup>1)</sup> This arrangement was already used in the determination of the heat of vaporisation of hydrogen, cf. Comm. N<sup>o</sup>. 137e.

<sup>2)</sup> The distances of the points of  $p_{i2}$  and  $p_{u1}$  (fig. 7) above, and below the respective mercury surfaces (covered with paraffin oil partly for suppressing the opening spark) are small and are made equal to each other by adjusting the mercury cups, whereas the velocity of fall of the two beams  $j_i$  and  $j_u$  was also made as equal as possible. The two other cups (see  $p_{i1}$  and  $p_{u2}$ ) may serve to use the apparatus as a switch-over key (e.g. if the same wire has to be used as a heating and as a thermometer wire, cf. § 3 at the end); in the present experiments they were not filled with mercury.

closes, respectively opens in passing its equilibrium position a current which operates a relai  $Q$ . This closes, respectively opens a current, which makes the bell  $L$  give a stroke every two seconds; this is registered by the telegraphic apparatus  $T$  the Morse-key  $M$  being in its position of rest. If, after contact has been made at  $i$  by a plug,  $M$  is pressed down at a moment that no current goes through (to be recognized from the position of the tongue of the bell), at the next closing of the current by the relai the beam  $j_i$  of the contact-key  $S_i$  (see Fig. 7) will be released, the platinum wire  $p_{i2}$  will fall into the mercury, and the heating current through the constantin wire will be closed<sup>2)</sup>. The switching out is operated in the same way by  $S_u$

for the measurement of the resistance is also represented. The galvanometer was of the DIESELHORST type with a period (undamped) of 4 sec. Before a calorimetric determination the resistance was measured, and the deflection of the galvanometer for a definite change in the ratio of the branches in the THOMSON bridge, the "sensitivity", determined. Then with a definite ratio of the branches the movement of the galvanometer (Fig. 3 and 4) was followed during the experiment. After this the measurements of the resistance and of the sensitivity were repeated. The current for measuring the resistance was 5 milliamperes. The heating current was for the lead 30 to 50, for the copper 12 to 27 milliamperes. Considering the ratio between the resistances of the thermometer and the heating wires the development of heat in the temperature measurement does not come into account.

We gladly record our cordial thanks to Dr. G. HOLST and Mr. P. G. CATH for the aid they afforded us in undertaking the temperature measurements.

Account had to be taken of the circumstance, that the reduction factor, which gives the ratio between the galvanometer current in the THOMSON bridge and the difference between the measured resistance and the resistance which would give no deflection, depends on the resistance in the variable branches of the bridge. A correction for this was always applied.

§ 3. *The resistance thermometer.* For the resistance thermometer a gold wire was chosen, as in the range of the measurements (14—90° K.) gold is more suitable for interpolation than platinum<sup>1)</sup>, and as on the other hand the indications of the gold thermometer are constant, if it is suitably treated before use (glowing before winding, then repeatedly cooling in liquid hydrogen and returning to room temperature). Before each series of measurements the constancy of the resistance of the wire was tested by a measurement at the boiling point of hydrogen.

In the temperature range of liquid hydrogen the gold thermometer was calibrated with the aid of a hydrogen vapour pressure apparatus as used in Comm. N°. 137*d*. The temperatures were deduced from formula (1) of that paper. In this way the scale of the gold thermometer is reduced to that of  $Pt_{17}$ , which has been once more accurately fixed by the research of KAMERLINGH ONNES and HOLST (Comm. N°. 141*a*). In the range of liquid oxygen this was done with the aid

<sup>1)</sup> H. KAMERLINGH ONNES and G. HOLST. Comm. N°. 142*a* (June 1914).

of auxiliary thermometers of platinum and of gold which had been compared directly with  $Pt_I$ .

The data for the gold thermometer  $Au_{c_1}$ <sup>1)</sup>, which was used in the measurements of May—June 1913 (table IV), were inserted in Comm. N<sup>o</sup>. 142a § 4e. Table I contains the data for the gold thermometer  $Au_{c_3}$ , which was used in June—July 1914.

TABLE I.

$T$	Resistance of $Au_{c_3}$ <sup>2)</sup>		Resistance of constantin <i>Const.</i> $c_3$	
		$W-R_I$		$W-R_{II}$
14.16°K.	0.6148	0.00	0.00	136.621
15.79	6286	— 10	+ 1	918
17.00	6419	— 14	0	137.138
17.96	6542	— 14	0	312
19.35	6749	— 8	0	565
20.31	6911	0	0	743
20.48	6946	— 0 <sup>5</sup>	— 3	776
68.22	2.6093			143.388
78.28	3.0917			144.000
90.27	3.6549			656

We also communicate in table II the calibration data of a gold thermometer  $Au_{c_2}$ , which became defective in some measurements concerning the specific heat of aluminium.

In connection with a remark by ZERNIKE in a paper published in these Proceedings, viz. that the resistance of  $Au_{c_1}$  (Comm. N<sup>o</sup>. 142a § 4e) for the range of hydrogen temperatures can be represented fairly accurately by a formula

$$W = a + b T^4 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

we have inserted under  $W-R_I$  in the tables I and II the differences between the observed temperatures and those calculated from the resistances with the formulae:

$$W = 0.5912 + 5.871 \cdot 10^{-7} \cdot T^4 \quad (Au_{c_3}) \quad . \quad . \quad (2a)$$

$$W = 0.07279 + 1.0974 \cdot 10^{-7} \cdot T^4 \quad (Au_{c_2}) \quad . \quad . \quad (2b)$$

In Fig. 8 we have represented besides these deviations (indicated by squares and triangles respectively), also those of  $Au_{c_1}$  (indicated by circles), for which  $T$  was calculated from

<sup>1)</sup> Wire of 0.05 mm. of HERAEUS.

<sup>2)</sup> Wire of 0.1 mm. furnished in January 1914 by HERAEUS.

TABLE II.

Resistance of $Au_{C_2}$ <sup>1)</sup>				
N <sup>o</sup> .	$T$	Resistance	$W-R_I$	
In liquid hydrogen with vapour pressure apparatus				
9 Dec. '13 II	14.25	0.07731 <sup>5</sup>	0.00	
III	14.95	7831	— 3	
IV	16.02	8019	— 9	
V	17.05	8232	— 12	
VI	18.01	8461	— 11	
8 Dec. I	18.04	8466	— 9 <sup>5</sup>	
9 > VIIa	19.36	8838	— 5	much liquid } in little .. } vapour } pressure } apparatus.
b	19.36 <sup>5</sup>	8839 <sup>5</sup>	— 5 <sup>5</sup>	
VIII	20.36	9165	0	
in liquid oxygen with $Pt_F$				
16 Dec. IV	59.00	0.4392		
III	77.84	6552		
15 > II	86.41	7517		
16 > II	86.43	7519		
15 > I	90.20	7941		
16 > I	90.30	7962		

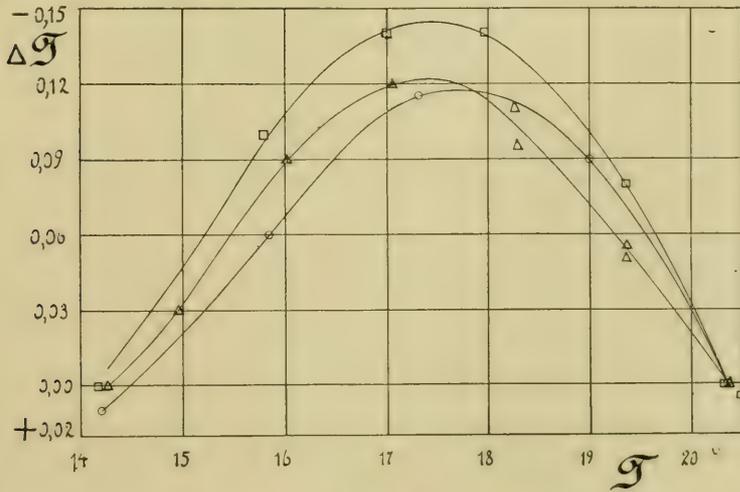


Fig. 8.

<sup>1)</sup> Wire of 0.1 mm. of HERAEUS.

$$W = 0.2691 + 5.425 \cdot 10^{-7} T^4 \quad (Au_{c_1}) \quad . \quad . \quad (2c)$$

These deviations are certainly not large (at most rather more than 0.1 degree); they are, however, appreciably larger than the inaccuracy of the measurements. They are on the whole larger as the impurity of the wire (as estimated by the ratio  $\frac{a}{b}$ ) increases. This increase of the deviations with increasing impurity seems, however, not to be strong enough to warrant the conclusion, that for pure gold proportionality of the resistance with  $T^4$  within the limits of the accuracy of the measurements would exist in the hydrogen region. This will find its expression in ZERNIKE's more general interpolation formula in the fact, that in this range the coefficients of the polynomial in the denominator already make their influence felt. GRÜNEISEN's relation  $W = C_p T$  brings this in connection with the deviation which the specific heat of gold shows in this range from the  $T^3$ -law<sup>1)</sup>.

In table I under  $W-R_{II}$  we have also inserted the deviations between the observed temperatures and those calculated from the formula:

$$W = 0.6879 - 0.01741 T + 0.000865 T^2. \quad (Au_{c_3}) \quad . \quad (3)$$

Practically this formula represents the resistance of  $Au_{c_3}$  accurately in this range, so that in the hydrogen range  $dW/dT$  depends linearly on  $T$ . Outside this range the formula would lead, however, to quite incorrect values<sup>2)</sup>.

For the calculation of the results of the calorimetric determinations dealt with in this paper graphic interpolation was made use of. For the hydrogen range graphs of  $W$  and of  $\Delta W/\Delta T$  were made on a sufficiently large scale according to the observed values. For the higher temperatures  $T$  and  $dW/dT$  were taken from graphs for the whole range of the calibration; for that purpose the  $W$ -curve was first drawn, from this values of  $dW/dT$  were taken for a

1) 8% at 20° K. if for gold  $t = 166$  is assumed according to DEBIJE.

2) We have also investigated whether the resistances of  $Au_{c_3}$  and  $Au_{c_1}$  (of which the first mentioned was enclosed in enamel, the second in paraffin) can be reduced to each other, either with the linear relation, which according to NERNST, or with the quadratic one, which according to HENNING exists between the values of the resistances of those wires corresponding to the same temperature. We found, however, that in the range from 14° to 90° K. both relations give deviations of several tenths of a degree between calculation and observation. The same result as regards NERNST's rule was found recently by H. SCHIMANK, Ann. d. Phys. (4) 45 (1914), p. 706. As regards the exceptional difference between observation and calculation in the case of  $Au_{VI}$  which was found by this physicist, we refer to the erratum given in Suppl. No. 19 (May 1908); in Comm. No. 99c p. 22 table I column  $Au_{VI}$  for 0.16822 is to be read 0.25234.

number of points in the range between hydrogen and oxygen temperatures, and these values were then smoothed graphically in the  $dW/dT$ -figure.

Together with the gold wire we accurately calibrated each time the constantin wire which was to serve for the heating, in order that this wire might serve as thermometer also (cf. p. 904 note 2) in case the gold wire should become defective. The corresponding data are given in Comm. N<sup>o</sup>. 142a § 4d and in this paper table I.

§ 4. *Heat capacity of the core.* This was measured separately in

TABLE III.

Heat capacity of the core $K_{III}$			
No.	Mean temperature	Increase of temperature	Heat capacity in Joules / degree
10 June II	14.61° K.	0.763	0.727
III	15.28	1.123	0.785
IV	16.19	0.992	0.887
V	17.37	1.149	1.019
VI	18.28 <sup>5</sup>	0.964	1.155
VII	19.11 <sup>5</sup>	0.867	1.288
I	20.10 <sup>5</sup>	1.288	1.530
VIII	20.16	1.048	1.406
IX	21.13	0.938	1.565
X* <sup>1)</sup>	28.37 <sup>5</sup>	0.979	2.99
XI*	29.00	0.927	3.17
XII	36.40	0.675	5.04
XIII*	46.32	0.509	8.19
13 June II*	61.87	0.503	12.91
III*	62.16	0.490	13.22
IV	70.33	0.429	15.39
V	70.74 <sup>5</sup>	0.417	15.58
I*	80.36	0.346	18.74
14 June I	80.51 <sup>5</sup>	0.318	17.87
II	80.88	0.356	18.56

<sup>1)</sup> For the measurements marked by an \* the calculation of the increase of

the same way as described in the preceding §§ for the block of metal and core together. We only communicate the results of the measurements for the core  $K_{III}$  which served for the measurements of June/July 1914 (table III).

§ 5. *Lead.* With lead ("KAHLBAUM") 3 series of measurements were made. The results of the first two series (1913) have been united in table IV, that of the last series (1914) in table V. Weight of the lead block: for the measurements of table IV: 715,6 grammes, for those of table V (the same block after removal of a layer at the surface) 709.7 grammes.

The measurements of 1914 must be considered as more accurate

TABLE IV.

Atomic heat of lead						
No.	Mean temperature	Increase of temperature	Heat capacity block + core in Joules/degree	id. core	Atomic heat in cal. <sub>15</sub> $C_p = C_v$	
16 May '13	II	14.96° K.	0.66	23.79	0.28	1.62
	III	15.86	0.73 <sup>5</sup>	27.27	0.33	1.86
	IV	16.62 <sup>5</sup>	0.67	29.75	0.37	2.03
	V	17.38	0.81	31.37	0.42	2.14
	VI	18.19	0.73 <sup>5</sup>	33.85	0.49	2.30
	VII	18.98	0.84 <sup>5</sup>	35.46	0.58	2.41
	VIII	19.81	0.80 <sup>5</sup>	37.20	0.69	2.52
	5 June '13	I	15.00	0.73 <sup>5</sup>	24.73	0.29
II		15.71	0.79 <sup>5</sup>	27.11	0.32	1.85
III		16.43	0.71	30.37	0.36	2.07
IV		17.22	0.84	31.58	0.41	2.15
V		18.16	0.78	34.73	0.49	2.36
VI		19.10	0.95	36.68	0.59	2.49
VII		20.10 <sup>5</sup>	0.95	36.78	0.74	2.49

temperature was not based on the determinations of the sensitivity (§ 2) immediately before and after those measurements, as in this case irregularities appeared to have occurred which have not yet been explained, but on an average value of the sensitivity, which was deduced for a number of successive measurements to which these belong. Apart from these irregularities the individual values for the sensitivity in one series of measurements did not differ as a rule by more than 2 to 4% (occasionally by 6 %).

than those of 1913. Nevertheless the latter are also communicated, as they confirm the conclusions to be drawn from the others.

$C_v$  was derived from  $C_p$  with the aid of the relation given by NERNST<sup>1)</sup> for lead:

$$C_p - C_v = 3,2 \cdot 10^{-5} T C_p^2.$$

In fig. 9  $C_v$  is represented according to the observations of 1914; fig. 10 gives a representation for the range of the hydrogen tem.

TABLE V.

Atomic heat of lead.						
No.	Mean temperature	Increase of temperature	Heat capacity lead block + core in Joules/degree	Atomic heat in cal. <sub>15</sub>		$\theta$
				$C_p$	$C_v$	
23 June '14 XIV	14.19° K.	1.106	23.08	1.56	1.56	85.7
III	15.31 <sup>5</sup>	0.927	26.83	1.81 <sup>5</sup>	1.81 <sup>5</sup>	85.9
IV	16.27 <sup>5</sup>	0.980 <sup>5</sup>	29.42	1.99	1.99	86.6
V	17.24	1.001	32.18	2.17	2.17	86.9
VI	18.25 <sup>5</sup>	1.008	35.72	2.41	2.41	86.3
VII	19.27	1.054	37.56	2.53	2.53	88.2
VIII	20.30 <sup>5</sup>	1.073	39.57	2.66	2.66	89.5
II	22.31	0.962	44.58	2.98	2.97	89.9
IX	27.51	1.019	54.41	3.60	3.59	92.4
X	28.50	0.993	55.52	3.66	3.65	94.0 <sup>5</sup>
XI	36.49 <sup>5</sup>	1.061	69.33	4.47	4.45	90.5
XII	45.61 <sup>5</sup>	0.469	77.53	4.85	4.81	
XIII	46.25	0.907	80.50	5.04	5.00	87.9
24 June I	57.20	0.476	89.47	5.43	5.38	
II	58.00	0.804	88.93	5.37	5.32	88.5
III	69.28	0.676	92.19	5.37	5.31	
IV	69.97	0.723	92.82	5.40	5.34	
V*1)	80.36 <sup>5</sup>	0.661	101.07	5.77	5.70	
VI*	80.86 <sup>5</sup>	0.671	99.82	5.67	5.60	90.1

1) W. NERNST. Ann. d. Phys. (4) 36 (1914), p. 426.

peratures separately, the observations of 1913 ( $\Delta\Delta$  and  $\gamma\gamma$ ) being also included.

In these figures the curve, which according to DEBIJE represents the atomic heat, calculated with  $\theta = 88$ , which value was derived by EUCKEN and SCHWERS from their measurements on lead, is also represented. In agreement with EUCKEN and SCHWERS we find that the observations show a good concordance with DEBIJE'S formula over the whole range. This concordance is, however, not complete; deviations show themselves which exceed the uncertainty of the results

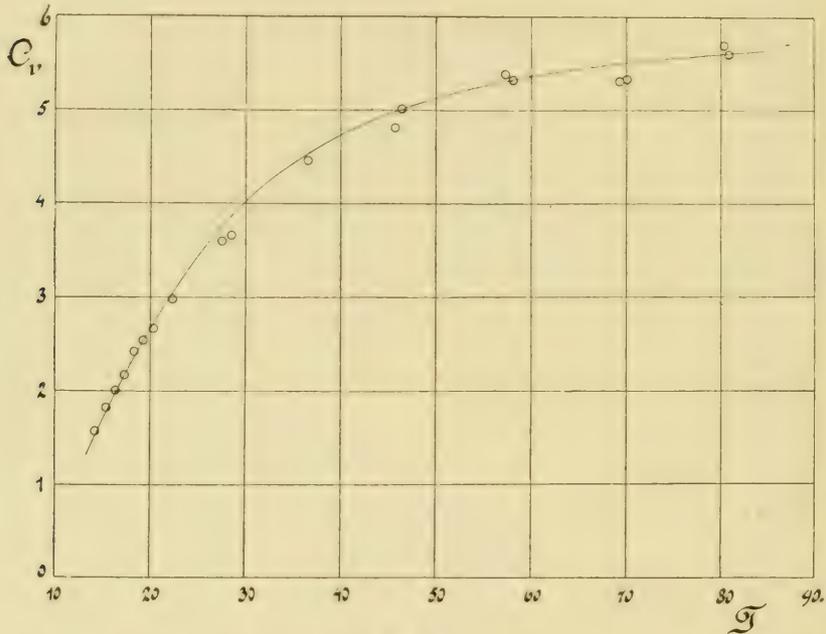


Fig. 9.

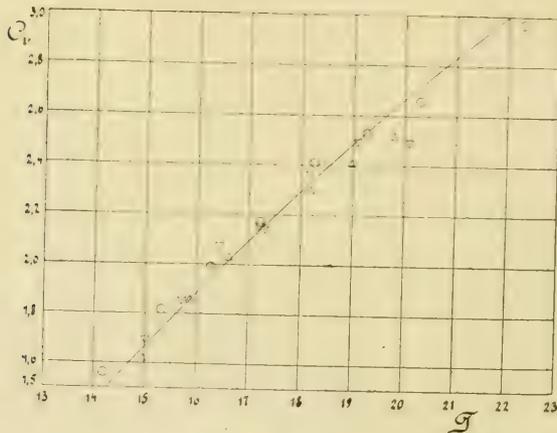


Fig. 10.

of the observations <sup>1</sup>). This appears to be the case in the first place in the range of hydrogen temperatures: the curve which unites the experimental results crosses the curve calculated according to DEBIJE (Fig. 10), in such a way that at 14° K. the specific heat is greater, at 20° K. it is smaller than the value calculated with  $\theta = 88$ . These deviations continue in the lower part of the range between hydrogen and oxygen temperatures, and decrease again in the higher part. It is true that the drawing of a conclusion is made uncertain in this region by the interpolation, which the gold thermometer requires there. We do not, however, consider it probable, that the deviations in this region are to be ascribed to the inaccuracy of the interpolation: 1. as they are a regular continuation of the deviations in the hydrogen region which are established with certainty, 2. as there are no indications that the deviations have a different sign in one part of the region of interpolation than in the other, as would have been the consequence of an inaccurate interpolation with the method of interpolation used (§ 3).

We are therefore led to the conclusion that the specific heat of lead shows deviations from the curve calculated according to DEBIJE, which unites the determinations at oxygen and at hydrogen temperatures in the best possible way ( $\theta = 88$ ), in the intermediate range of the temperatures, to the extent of about 4% at 30° K. (cf. also table VI).

These deviations may presumably find their explanation in one or more of the following circumstances: *a.* that we did not observe with a homogeneous substance crystallized in the regular system, but with a micro-crystalline aggregate consisting of different phases, such as the two different states of crystallisation assumed in superconductors for the explanation of the micro-residual resistance (Comm. N<sup>o</sup>. 133 § 11), which perhaps also come into play in the experiments of COHEN and HELDERMAN <sup>2</sup>), who on the ground of their investigations assume, that with lead we are dealing with a metastable complex of two or more modifications, *b.* that the approximate suppositions concerning the elastic spectrum made in DEBIJE's theory

<sup>1</sup>) At the points  $T = 57.20, 69.28$  and  $69.97$  the irregularities mentioned in note 1 p. 905 in the determination of the sensitivity have presumably also occurred, though in a less degree. The first point has probably been calculated with too large, the last two with too small a value for the sensitivity.

<sup>2</sup>) E. COHEN, These Proc. June 1914, p. 200; E. COHEN and HELDERMAN, These Proc. Nov. '14, p. 822. COHEN l. c. quotes measurements of LE VERRIER according to which at 220 to 250° C. lead would pass into another modification with appreciably larger specific heat (at constant pressure). The measurements by P. SCHÜBEL, Zs. f. anorg. Chem. 87 (1914), p. 81, do not, however, confirm this result.

are not strictly valid,  $c$ , in a change with the temperature of the quantity  $\theta$  which occurs in that theory, in other words of the elastic properties of the material<sup>1)</sup>.

Concerning  $b$  it may be remarked that for a substance which should crystallize in the simplest cubical space-lattice THIRRING has derived an expression for the specific heat from the theory of BORN and v. KÁRMÁN which in consequence of the more rigorous consideration of the molecular structure followed in this theory might give a nearer approximation to the actual conditions. It is true that for a thorough discussion in connection with THIRRING's deductions the data about the elastic constants in the temperature region considered are as yet wanting. Without these we can, however, establish the following facts.

In table VI are given besides the deviations ( $W-R_D$ ) between the

TABLE VI.

$T$	$C_v$	$W-R_D$ ( $\theta = 88$ )	$W-R_{Th_1}$ ( $\theta_{Th_1} = 67.5$ )	$W-R_{Th_2}$ ( $\theta_{Th_2} = 68$ )
14.19	1.56	+ 0.085		
15.31 <sup>5</sup>	1.81 <sup>5</sup>	+ 8 <sup>5</sup>		
16.27 <sup>5</sup>	1.99	+ 6		
17.24	2.17	+ 5	+ 0.26	
18.25 <sup>5</sup>	2.41	+ 8	+ 28	
19.27	2.53	0	+ 19	
20.30 <sup>5</sup>	2.66	- 7	+ 11	
22.31	2.97	- 7 <sup>5</sup>	+ 4	
27.51	3.59	- 15	- 10	
28.50	3.65	- 20	- 16	- 0.20
36.49 <sup>5</sup>	4.45	- 8	- 7	- 7
46.25	5.00	0	0	+ 1
58.00	5.32	- 1	- 1	- 1

observed values of  $C_v$  and those calculated according to DEBIJE with  $\theta = 88$ , also the deviations  $W-R_{Th_1}$ , between the observations and the values calculated from a series given by THIRRING:

<sup>1)</sup> In determining this influence it should be borne in mind that, as is specially pointed out by EUCKEN, Verh. d. D. physik. Ges. 15 (1913), p. 571, the elastic properties must have been measured on homogeneous crystalline material.

$$C_v = 3R \left\{ 1 - \frac{B_2}{2!} \left( \frac{\theta_{Th}}{T} \right)^2 + 3 \frac{B_4}{4!} \left( \frac{\theta_{Th}}{T} \right)^4 - 5 \frac{B_6}{6!} \left( \frac{\theta_{Th}}{T} \right)^6 \dots \right\}, \dots \quad (4)$$

in which  $B_1, B_2 \dots$  are the Bernoullian coefficients and  $\theta_{Th}$  is a constant. Apparently the agreement of the observations with DEBIJE's formula is closer than that with this series of THIRRING.

It deserves further to be noticed, that this series can only be derived from the theory of BORN and v. KÁRMÁN by the introduction of imaginary values for the elastic constants (assuming that they are independent of the temperature). From the series which THIRRING derives from the theory mentioned above:

$$C_v = 3R \left\{ 1 - \frac{B_2}{2!} J_1 \left( \frac{h}{kT} \right)^2 + 3 \frac{B_4}{4!} J_2 \left( \frac{h}{kT} \right)^4 \dots \right\}, \dots \quad (5)$$

where  $J_1, J_2 \dots J_4$  represent definite functions<sup>1)</sup> of the elastic constants  $c_{11}, c_{44}, c_{12}$ , introduced by VOIGT, the following series may be derived as the one which at the higher temperatures approaches nearest to series (4)<sup>2)</sup>:

$$C_v = 3R \left\{ 1 - \frac{B_2}{2!} \left( \frac{\theta_{Th}}{T} \right)^2 + 1,1 \cdot 3 \frac{B_4}{4!} \left( \frac{\theta_{Th}}{T} \right)^4 - 1,278 \cdot 5 \frac{B_6}{6!} \left( \frac{\theta_{Th}}{T} \right)^6 + \right. \\ \left. + 1,6393 \cdot 7 \frac{B_8}{8!} \left( \frac{\theta_{Th}}{T} \right)^8 \dots \right\} \dots \quad (6)$$

Under  $W-R_{Th_2}$  in table VI are given the deviations between the observations and the values calculated from (6) with  $\theta_{Th_2} = 68$ . It appears that THIRRING's formula (5) with the special assumptions concerning the elastic constants for which it passes into (6), in the region for which the coefficients have been developed by him, practically coincides with DEBIJE's formula. Whereas, when the elastic constants do not agree with those assumptions, THIRRING's formula deviates from DEBIJE's formula in a direction opposite to the observations.

Hence we come to the conclusion that a closer consideration of the molecular structure in the sense in which it is done in the theories of BORN and v. KÁRMÁN and of THIRRING, at least on the assumption of the arrangement in the simplest cubic space-lattice, does not account for the deviations indicated above.

It remains either to consider an arrangement in one of the other space-lattices of the regular system<sup>3)</sup>, or to assume that one or both of the

<sup>1)</sup> H. THIRRING, Physik. Z. S. 14 (1913), p. 870 and 15 (1914), p. 181 note 1.

<sup>2)</sup> This would require  $c_{11} = \frac{3}{2} c_{44}, c_{12} = 0$ .

<sup>3)</sup> A comparison with the deduction by BORN, Ann. d. Phys. (4) 44 (1914), p. 607 of  $C_v$  for the space-lattice as deduced by BRAGG for diamond (also a regular crystal) leads, however, to quite analogous results as are given above for the simplest cubic space-lattice.

circumstances mentioned above under  $a$  and  $c$  also play a part<sup>1)</sup>. The latter of these, viz. a change of the elastic properties with the temperature, would be connected with deviations from the linear relation between the forces between the molecules and their relative displacements, which deviations DEBIJE<sup>2)</sup> also makes responsible for the thermal expansion.

In table V are given the values of  $\theta$ , which are obtained by applying DEBIJE's formula for  $C_v$  to the individual observations. They are united in Fig. 11<sup>3)</sup> 4).

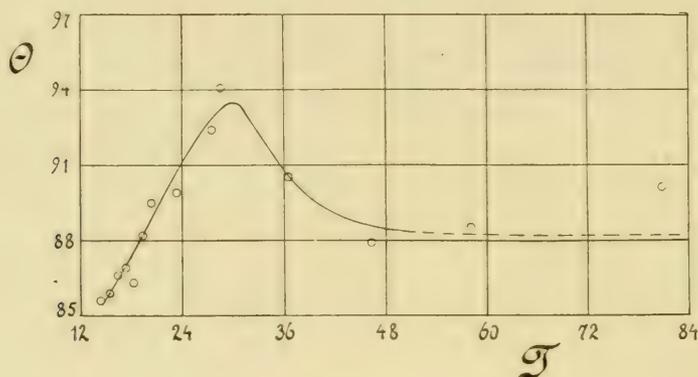


Fig. 11

§ 6. *Copper.* With copper we were as yet only able to make a series of measurements between 15 and 22° K. The copper was electrolytic copper of FELTEN and GUILLAUME, 596,0 grammes.

$\bar{C}_v$  in table VII represents the mean atomic heat between the initial and final temperatures; for correction to the "true" atomic

<sup>1)</sup> Regarding  $a$  it may still be remarked that the presence of a second modification of appreciably different properties in a considerable quantity would lead us to expect much larger deviations from DEBIJE's formula than appear actually to exist. If the circumstance mentioned under  $a$  plays a part, we therefore have to assume a small quantity of a second modification, or a second modification whose elastic properties are only little different from those of the first.

<sup>2)</sup> P. DEBIJE, Vorträge Wolfskehlcongres Göttingen 1913.

<sup>3)</sup> The slow change, which EUCKEN and SCHWERS l.c. observed in the values of  $\theta$  for lead as derived from their measurements, and which does not coincide with that found by us, is considered by them as probably due to the uncertainty of the temperature coefficient of their resistance thermometer.

<sup>4)</sup> Fig. 11 gives a special illustration of the character of the deviations from DEBIJE's formula over the whole range, and can also serve to calculate a smoothed value of  $C_v$  by reading the value of  $\theta$  corresponding to a definite  $T$  from the smoothed curve. At the same time it should be remarked, that the values of  $\theta$  represented in Fig. 11 do not coincide with  $h\nu_{max}/k$ , if  $\nu_{max}$ , the maximum frequency according to DEBIJE, changes with  $T$ .

heat  $C_p = C_v$  corresponding to the mean temperature of the measurement use was made of the proportionality  $C_v \sim T^3$ , which appears to be valid in this region.

Table VIII contains the comparison of the experimental values

TABLE VII.

Atomic heat of copper.					
N <sup>o</sup> .	mean temp.	increase of temperature	heat capacity copperblock + core in Joules/degree.	Atomic heat in cal <sub>15</sub> .	
				$\bar{C}_p$	$C_p = C_v$
3 July '14					
II	15.24° K.	4.222	2.748	0.0500	0.0491
III	17.50	0.920	3.895	726	726
IV	18.03	0.842	4.222	792	792
V	18.89	0.726	4.884	930	930
VI	19.58	0.606	5.305	1010	1010
VII	20.88	1.355	6.417	1248	1247
I	21.50 <sup>5</sup>	2.156	7.159	1414	1410

TABLE VIII.

Atomic heat of copper.					
T	$C_v$	$\theta$	$C_{v\text{calc.}}$ ( $\theta = 323.5$ )	Obs.—Calc.	
					in %
15.24	0.0491	322.3	0.0486	+ 0.0005	+ 1.0
17.50	726	324.9	735	— 9	— 1.2
18.03	792	325.2	804	— 12	— 1.5
18.89	930	322.9	925	+ 5	+ 0.5
19.58	1010	325.6	1030	— 20	— 1.9
20.88	1247	323.7	1249	— 2	— 0.2
21.50 <sup>5</sup>	1410	320.0	1365	+ 45	+ 3.3
		mean 323.5			

with the relation given by DEBIJE for sufficiently low temperatures:

$$C_v = 77,94 \cdot 3 R \left( \frac{T}{\theta} \right)^3 \dots \dots \dots (7)$$

The column headed  $\theta$  contains the values of  $\theta$  calculated according to formula (7) from the individual measurements.

From these measurements the conclusion can be drawn, that in the temperature range from 15 to 22° K. the specific heat of copper follows DEBIJE'S  $T^3$  law within 2 %<sup>1)</sup>.

**Anatomy.** — “*A case of occlusion of the arteria cerebelli posterior inferior.*” By Prof. C. WINKLER.

(Communicated in the meeting of November 28, 1914).

J. P., aged 58, artisan-painter, has never before shown any other irregularities but palpitations after physical exertion before the beginning of his illness on October 20<sup>th</sup> 1912.

At the age of twelve he became an apprentice-painter, and always afterwards kept to this handicraft. As a young man he used to smoke much, and also drank much beer, but he firmly denies any sort of venereal infection, though he underwent a treatment for strictura urethrae at the age of 45. His father died of consumption, his mother of jaundice. The eldest *sister* died of apoplexy. The patient is the sixth among nine children. He married young and has five healthy children.

At eight o'clock in the morning of the 20<sup>th</sup> October he *suddenly complained of dizziness* and was obliged to sit down on a chair. He *did not lose consciousness*, but could no longer walk because his *right leg had become lax*. He could neither *speak* nor *swallow*, and suffered of double vision.

Before the beginning of this attack he had walked for a quarter of an hour over hilly ground, and for the rest had even kept himself unusually quiet.

For this attack of vertigo he was treated in the hospital at Pretoria. *After a fortnight* he was *again able to speak in so far as to make himself intelligible*, although he never completely recovered his voice; *swallowing* too was *performed normally again* at this time.

After *two months* he began to walk about again with the aid of a stick. Since the attack however his sense of taste had suffered much. After *three months* the *double vision* had disappeared too.

He did not suffer from *headache* either before or during the attack of vertigo. Neither had there been *any vomiting*, nor *singultus*.

It left however some lasting symptoms, to wit:

1. formications (needle-prickings) in the right half of the body and in the left half of the face.
2. his right eye seemed to him to be covered by a film.
3. he (is) was unable to distinguish between cold and heat with his right hand.

1) Later, more accurate measurements, which however have not yet been completely finished, seem to show that in this region a small deviation from the  $T^3$ -law exists which slightly surpasses the amount mentioned above. [Added in the translation].

4. he is unable to walk without a stick, because he often feels suddenly dizzy.

5. he cannot look quickly sideways, without losing his equilibrium.

6. when looking suddenly sideways (especially to the right), he cannot recognize the objects standing beside him, at least not immediately.

For the rest the patient declares that his hearing was bad since long. Eating, drinking and sleeping are all right. No disturbances in the deposition of the urine or in defecation.

*Status praesens.* A strongly built man, average height, good nutrition, well-fed. Colouring of the skin and mucous membranes healthy.

The left *arteria temporalis* is visibly crumpled, its wall has surely doubly the thickness of that on the right. To the touch it seems to be tense.

The tongue is moist, not coated. Nowhere any swelling of glands.

Pulse 90 per minute, regular and equal.

Breathing abdominal, 24 per minute, regular.

Heart under percussion normal, under auscultation a slightly accentuated diastolic sound in the aorta. Lungs normal both under percussion and auscultation. No irregularities are to be stated in the abdomen. Urine: acid reaction — no albumen, no glucose.

The local sense of J. P. is good, he knows that he is in the Binnengasthuis, is aware too of the right date. His surroundings do not however interest him much.

His memory is good. A number of six figures is correctly reproduced after a lapse of five minutes. Simple and even somewhat more complicated arithmetical questions are correctly solved mentally, e. g.  $13 \times 14 = 182$ .

The internal speech is unimpaired.

The external speech is rather monotonous, lacking articulation.

The voice is hoarse.

Reading presents no difficulties, neither does writing, which is done in a very neat hand.

The hair-covering of the head is normal, as are likewise the boundaries of the hair-growth. *The head is ever kept turned somewhat to the right.* The face is asymmetrical. The *left cheek* is thicker than the right one, it *feels hotter to the touch and is injected.* The left regio temporalis is salient. The *left orbital fissure* is narrower than that to the right. The *left bulb* is slightly directed upward.

The circumference of the head is 59 cm.

Not unfrequently an *involuntary movement* may be observed, by which *the head* is thrown *to the right.* The eyes then are turning first to the left and afterwards follow slowly the movement of the head to the right.

The nerves of the brain:

I. *Olfactorius.* The patient states that his sense of smelling was enfeebled long before his illness. To the left he recognizes neither Eau de cologne nor anisseed-oil.

II. *Opticus.* Visus (after correction of the hypermetropy + 3 D) on both sides I. The fundus is normal on both sides, as is likewise the field of vision.

III, IV, V. Movements of the eye. *The pupil* on the left side is *somewhat narrower* than that on the right, the latter is of normal width. On both sides the pupils are reacting on light and on convergency. *The orbital fissure to the left is narrower than that to the right. The left bulbus is slightly protruding.*

The position of the bulbi is somewhat diverging. When in rest, sometimes *nystagmoid movements* appear, usually to the left and in horizontal direction.

They disappear when the patient regards fixedly. *In darkness nystagmus to the left.*

The *convergency is normal*, the right bulbus however deviates soon towards the left. *No double vision.*

The *moving of the two bulbi* is normal to the right, to the left it is accompanied by *nystagmus*, which however soon ceases afterwards, the moving of the two bulbi upward and downward is likewise complicated by nystagmus.

Besides this there is no paralysis of the muscles of the eye.

When the patient is looking straight forward, and is summoned to regard fixedly anybody standing on the right of him, he does so in the following manner: He turns his head to the right; both eyes remain behind in this movement, they are even drawn towards the left for one moment, it is only after this that they are following slowly the movement of the head, and that the patient looks fixedly into the desired direction.

V. The N. trigeminus. All motor functions of mastication etc. are undisturbed. Sensibility on the contrary has suffered.

The *tactile sense* is unimpaired on both sides. Every contact, however slight, with a hair-pencil or a small plug of cottonwool, is instantly perceived.

On the other hand the *perception of pain* is destroyed over the whole of the trigeminus-area on the left side. The difference between the head and the point of a pin is not distinguished. Nowhere at any point within this area is a painful contact perceived. To the right the sensibility to pain is intact.

The *perception of temperature*, intact to the right, is likewise disturbed to the left. On this side melting ice is still recognized to be cold, but as being less cold than to the right. With regard to the perception of heat, there is always a difference disfavoured to the left side. The boundary-line of the left analgesy (conf. the scheme) is distinctly defined against the median line, it then passes over the top of the head and returns behind the ear (which is included in the analgesia) along the chin to the median line, where it meets the analgetic right half of the body (conf. later on).

The left half of the mucous membrane of the cavity of the mouth is likewise analgetic, the boundary-line passing over the median line of the tongue and  $\pm$  over the middle of the palatum. The latter is swollen (conf. later on).

A deep impression is correctly perceived both to the right and to the left within the trigeminus-area. The two points of the compass of WEBER are well distinguished on both sides at a distance of  $\pm 20$  cm. (vertically). The sense of localisation is intact on both sides.

The cornea is normally sensible to the right. To the left both the pain-sensibility and the tactile sense have completely disappeared in it, and a piece of melting ice on the left cornea is not felt to be cold. The cornea-reflex is failing.

The left facial half is hyperaemic and swollen, it feels hotter to the touch, but there is no tropical abnormality.

VII. The N. facialis is intact on both sides. All mimical and voluntary innervation of the face is performed on both sides in the same manner.

VIIIa. The Nervus cochlearis. The tympanic membrane (observation of Dr. VAN GILSE) is normal to the right, and to the left it becomes normal too after the removal of a plug of cerumen.

The patient has not heard well to the right since long (before the attack of vertigo).

To the right upper limit of hearing by bone-conduction (monochord STRUYCKEN)  $15\frac{1}{2}$  (norm. 13—14).

Upper limit of hearing by air-conduction idem 31 (norm. 14).

To the left " " " " " bone-conduction idem  $15\frac{1}{2}$ .

" " " " " air-conduction idem 31.

Whispering voice. To the right  $\pm 8$  cm.

To the left low zone  $\pm 3$  cm.

high zone  $\pm 5$  cm.

To the right the patient does hear:

SCHWABACH shortened. WEBER not lateralized. RINNE to the left +, to the right —.

VIIIb. *The nervus vestibularis*. Injection of cold water.

On the right side it distinctly produces nystagmus to the left. Afterwards there is  $\pm$  no deviation to be found in both arms in pointing at a fixed object.

On the left side there is as distinctly produced nystagmus to the right. The pointing experiment made after this shows no deviation for the right arm, but it does so for the left arm that is deviating to the right.

IX, X, XI. The taste has not suffered either to the left or to the right. Subjectively the patient declares that his sense of taste has diminished on the tip of the tongue.

The uvula is swollen clubshaped at its end, on its right upperside there is a scar. It is deviating towards the right.

The arcus palatini to the right are placed lower than those to the left. On innervation both arches are lifted slightly (a result of the swollen uvula). Insignificant Rhinolalia aperta.

Laryngoscopically (Dr. VAN GILSE). Epiglottis abnormally small. *During phonation the right vocal cord is passing far over the median line*. Of the left vocal cord only a small margin is visible, half concealed under the swollen false vocal cord. *The left vocal cord is entirely motionless*, there are neither abductor nor adductor motions.

The motions of the right vocal cord are normal.

To the left there is tumefaction in the region of the arythenoid-cartilage and in the sinus piriformis.

*A complete paralysis of the left N. accessorius of the oblongata* is assumed to exist.

The shoulders are lifted without any difficulty. M. trapezoides and M. sterno-cleido-mastoidens are not atrophic.

Swallowing presents difficulties, because according to patient, there is an impediment to the left.

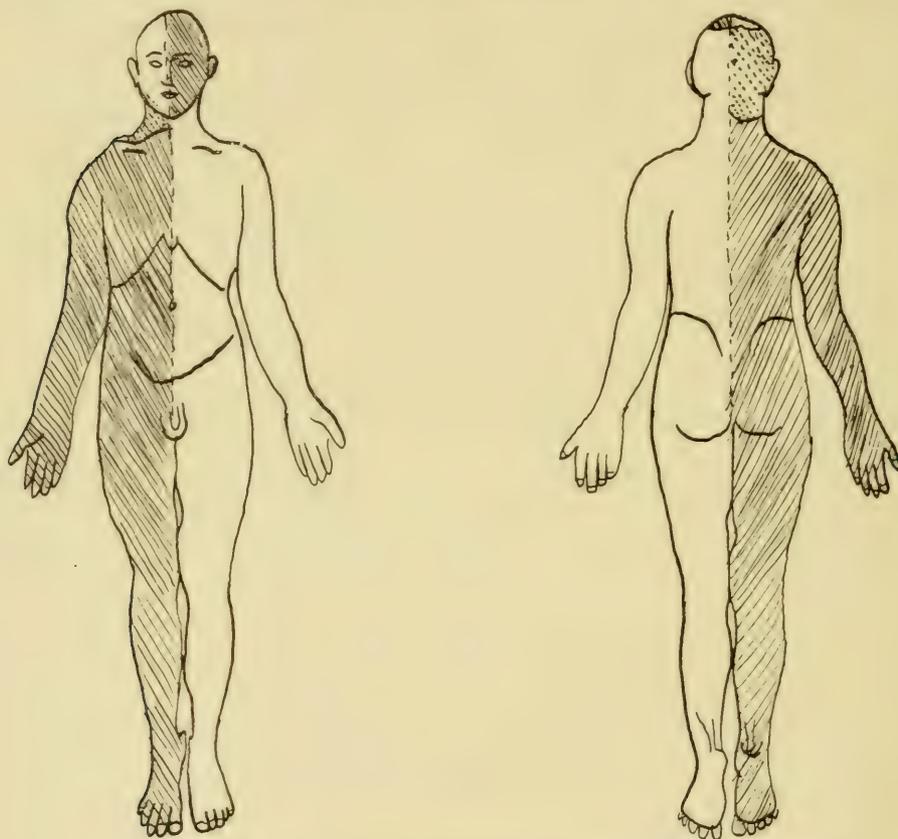
XII. *The N. hypoglossus*. When in repose the tongue is normal, when put out it is stretched straightforward. Strong tremor, especially at the tip. Movements can be made in all directions. The innervation of the bottom of the month is equal on both sides.

*Neck and trunk*. The attitude of the head is always turned to the right. For the rest no irregularities in the movements of neck and trunk. The vertebral column is nowhere painful. The patient is able to raise himself from a declining posture to a sitting one without the aid of his arms.

*Sensibility*. The tactile sense is undisturbed both to the right and to the left, even the slightest contact with a plug of cottonwool or a hair-pencil is instantly perceived.

On the contrary the *pain-sensibility is entirely destroyed on the right side* with distinct boundary-lines at the mid-ventral and mid-dorsal lines. Diminished in the region of the neck and at the right side of the occiput (see the dotted lines in the scheme), this incomplete disturbance is distinctly separate both from the complete analgesia of the trunk and from the normally sensible region of the trigeminus to the left.

*The sense for temperature has likewise completely disappeared on the right side.* No difference is felt between melting ice and hot water. A tube containing cold or hot water is called alternately cold and hot.



J. P. Aged 59. ///// Complete Thermo-anaesthesia and Analgesia.  
 : Incomplete Thermo-anaesthesia and Hypalgesia.  
 November 1914.

As soon however as the patient is touched *on the right side* with a hot object, he feels a *peculiar pricking sensation at the left exterior corner of the eye and at the left nostril.*

Further the reflex-actions of the abdomen and the cremaster exist on both sides.

*Arms.* On inspection no abnormality, well developed muscular system, normal tonus on both sides. All movements are performed powerfully with strength. The dynamometre points 85 on the Right, 65 on the Left. No ataxy when pointing with the index to the tip of the nose, or when the two indices are brought together. Normal diadokynesis. The reflex-actions are high on both sides.

The tactile sense is undisturbed on both sides.

*The perceptions of pain and of temperature are completely destroyed to the right (conf. the schema), to the right they are undisturbed.*

The nerve-trunks remain painless under pressure.

The perception of active and passive movements is particularly good. On both sides localisation is normal. The two points of the compass of WEBER are recognized and distinguished within the appointed scale. On both sides stereognosia is perfectly normal.

*Legs.* On inspection no irregularities, powerful muscular development with normal tonus. Neither tremor nor accessory movements.

All movements are executed on both sides powerfully and with equal strength. No ataxy of movement when the knee-heel experiment is made or when describing a small circle.

During repose however there is a *slight static ataxy*. When standing with both feet closely joined, the patient totters and threatens to fall, usually to the left. This becomes rather worse when his eyes are closed. The patient walks with legs wide apart, and generally deviates towards the left of his course. It is impossible for him to stand on one leg either on the left or on the right, and likewise to halt.

When walking, the trunk is borne somewhat stiffly.

The reflex-actions of the knee and of the tendo Achillis are normal on both sides.

Reflex-action of the plant of the foot to the right: plantar-flexion of all toes with averting movement.

To the left plantar-flexion of the little toes after irritation of the planta pedis, and when the tibia is stroked.

The *tactile sense* is undisturbed on both sides. Even the slightest contact is perceived.

*Pain-sensibility. Normal to the left.* On this side a frightened reaction, accompanied by a deep inhalation, repeatedly follows on a pin-prick, as if there existed a strong hyperaesthesia.

*Nowhere on the right is pain-perceived.* Although sometimes by an effort the patient is able to distinguish between the contact with the head or with the point of a pin, still this distinction is not founded on any perception of the sensation of pain.

*The exterior genitals are analgetic to the right,* though the boundarylines do not follow strictly the median line, but deviates somewhat towards the right.

*The perception of heat and cold is intact on the left, it has disappeared on the right.*

On both sides *passive and active movements* are perceived with absolute correctness. The *sense of space* is undisturbed on both sides. Localisation, though with a rather large declination, is good on both sides.

The state of the patient remained unchanged during the months of October and November. The reaction of WASSERMANN was found to be negative in the blood. Lumbar puncture was not performed.

Summing up, we may state the case as follows:

On the 20<sup>th</sup> of October 1912, at eight o'clock in the morning, accompanied by violent vertigo, but without loss of consciousness, a complex of symptoms presented itself, fitting into the general view of the so-called per-acute bulbar paralysis. Part of these symptoms

— the disturbances of speech, the difficulty in swallowing, the laxity of the right leg — have been soon meliorated or cured. Another part of them however have become lasting.

The most important of these residue symptoms are:

*a.* Complete analgesia and thermanaesthesia in those regions of skin and mucous membrane that are controlled by the *left N. trigeminus*, — the tactile sense, localisation and motor-power having been preserved in the trigeminus-muscles.

The reflex-action of the cornea no longer exists.

This analgesia alternates with:

*b.* Complete analgesia and thermanaesthesia in the right half of the body. Within the region of the upper cervical roots on the right this disturbance is incomplete. The tactile sense, the deep sensibility, the sense of space, localisation and stereognosy are undisturbed and have not suffered in the right half of the body. There is not one single symptom of hemiplegia.

*c.* Complete paralysis of the larynx to the left. Incomplete paralysis of the swallowing-muscles on that side.

*d.* A peculiar involuntary attitude of the head, turned towards the right, together with a dissociation of the conjugate movement of the eyes and the head turning to that side. When this movement is made, the eyes cannot follow it. They first turn towards the left, afterwards slowly following the movement of the head towards the right, the patient being consequently unable to recognize instantly the objects placed beside him, on account of the defective stand of the eyes.

*e.* A slight degree of static ataxy.

Without any doubt this disturbance is caused by an occlusion in the arteria cerebelli posterior inferior and a softening (eventually a cyst) in the latero-dorsal portion of the left half of the medulla oblongata.

This morbid affection has been first described and appreciated by SENATOR<sup>1)</sup>, subsequently it has been carefully analysed by WALLENBERG<sup>2)</sup> and MARBURG<sup>3)</sup>, who have done most meritorious

<sup>1)</sup> H. SENATOR. Zur Diagnostik der Nervenkrankungen in der Brücke und in dem verlängerten Mark. Arch. f. Psych. Bd. 14. 1883. p. 643 ff.

<sup>2)</sup> ADOLF WALLENBERG. Acute Bulbär-affection (Embolie der arteria Cerebellaris posterior inferior sinistra). Arch. f. Psych. Bd. 27. 1895 p. 504 ff. and:

WALLENBERG. Anatomischer Befund in einem als Embolie der art. cerebellaris posterior inf. sinistra beschriebenen Falle. Arch. f. Ps. Bd. 34. 1901. S. 928

<sup>3)</sup> R. BREUER und OTTO MARBURG. Zur Klinik und Pathologie der apoplectiformen Bulbärparalyse. Arbeiten aus dem neurologischen Institut der Wiener Universität (OBERSTEINER) Bd. IX. 1902. p. 181.

work for the pathology of the medulla oblongata. RUDOLF BRUN<sup>1)</sup> has given a nearly complete summary of the literature on this subject, into which I will not enter here.

The foregoing case has been communicated, because in a clinical sense it is a peculiarly well-defined case.

A few remarks I may be allowed to add still about it. Before the arteria vertebralis has united with the contra-lateral one to form the arteria basilaris, it supplies the medulla oblongata with several small branches. Among these branches the art. spinalis dorsalis

*Scheme of the Nutrient bloodvessels of the medulla oblongata after DURET.*

(Archives de Physiologie. 1873. Tome V. Planche VIII).

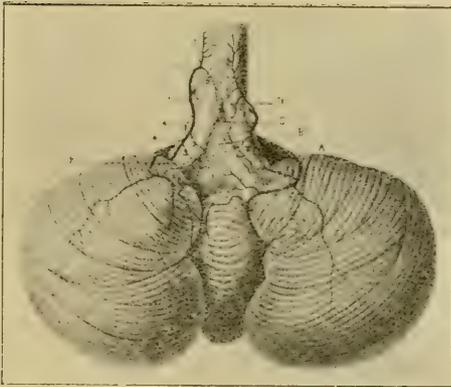
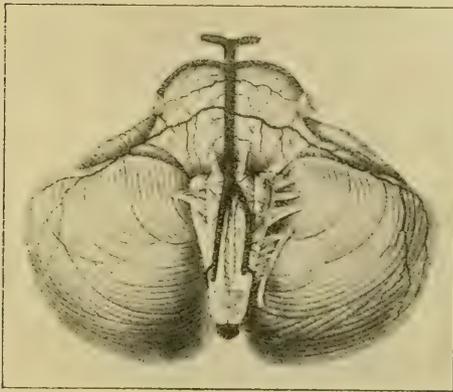


Fig. I. A. Art. cerebellaris posterior (inferior).

B. Art. cerebellaris media (inferior anterior).

C. Art. cerebellaris superior.

D. Art. cerebellaris posterior.

1. Art. radicularis (N. accessorii spinalis).

2. Art. spinalis anterior.

3. Art. radicularis (N. X et N. IX).

4. Art. auditiva spinalis (N. VII et N. VIII).

5. Art. radicularis N. VI.

6—7. Arteriae fossae supra-olivaris.

8. Arteria auditiva interna (from B).

9. Art. N. V.

10. Art. radicularis N. XII.

Fig. II. A. Plexus chorioideus.

B. Tela chorioidea.

C. Foramen Morgagni.

D. Clavus.

1. Arteria cerebelli posterior inferior.

2—4. Small branches of this artery.

5. Arteria spinalis posterior.

6—8. Small branches of this artery.

<sup>1)</sup> RUDOLF BRUN. Ein Fall von doppelseitigen symmetrischen Erweichungssystem im verlängerten Mark.

Arbeiten aus dem hirnanatomischen Institute der Universität in Zürich. Bd. VI. 1912. S. 270—400.

and the art. cerebelli posterior inferior are of especial interest to us. They originate on both sides from a joint small branch of the art. vertebralis on the anterior side of the oblongata. The art. spinalis dorsalis then descends along the lateral surface of the oblongata and provides for the caudal portion of the medulla oblongata. The art. cerebelli ascends between the corp. restiformis and the oliva inferior, it provides for the laterodorsal portion of the m. oblongata in its proximal part by means of small branches originating from it in perpendicular direction, and then leaves the corpus restiforme to supply further with blood the distal half of the basal cerebellum-laminae.

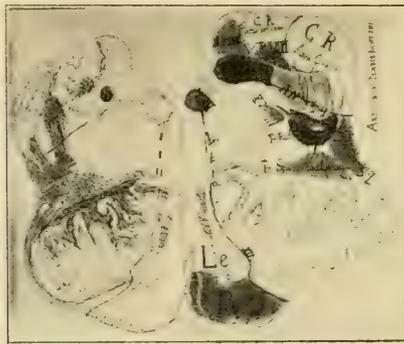
The area of irrigation of the art. cerebelli inferior posterior is accordingly situated within the latero-dorsal portion of the med. oblongata proximally to that of the art. spinalis dorsalis.

The N. octavus is lying proximal to this irrigation-zone.

The boundary line between pons and oblongata forms the proximal demarcation of this region, about there where the distal part of the nucleus N. VI is to be found. Caudally it is confined by the N. ambiguus, the caudal extremity of which is provided for by the art. spinalis dorsalis. The ventral boundary is indicated approximatively by the Oliva-nucleus; the dorsal one by the basal nuclei that have their own supply of arteries, the medial boundary by the nucleus and the roots of the N. XII.

Surveying a topographical map of the medulla oblongata, we may see that within the irrigation zone of the art. cerebelli posterior inferior are found:

Fig. III. Scheme of the area of irrigation of the art. cerebelli inferior hit by a frontal section.



*a.* That part of the tractus spinalis N. V, that is going in a caudal

direction opposite to the upper half of the oliva inferior. The sensible nucleus of this nerve and its motor nucleus are not included.

*b.* The so-called "aberrirendes Seitenstrangfeld", in which are found the spino-thalamic (EDINGER'S) tract, the rubro-spinal (MONAKOW'S) tract, and the ventral spino-cerebellar (GOWER'S) tract.

*c.* The proximal part of the N. ambiguus, i. e. the ventral nucleus of the N. IX, X, and partly too of the N. XI, besides the forth-coming roots of these nerves.

*d.* The interior portion of the Corpus restiforme (MONAKOW'S I. A. K.) with the descending root of the N. VIII that is found within it.

Besides, in the immediate vicinity of this region is lying the Nucleus dorsalis N. X, especially the tractus solitarius with its nuclei, and if medialward this region extends really so far as the radices N. XII demarcate the formatio reticularis grisea, then the tractus vestibulo-spinalis belongs likewise to it.

Moreover the caudal basal portion of the cerebellum must be also reckoned to belong to this irrigation zone.

According to the symptoms this dorso-lateral portion of the oblongata is destroyed on the left side.

As the most prominent disturbance there was found:

I. *Alternating paralysis of the sensibility for pain and for thermal stimuli, to the left in the region controlled by the N. V, to the right over the whole half of the body, with the exception of the Trigemini-area.*

The tactile sense, localisation and the sense of space, perception of passive and active movements, stereognosia, are all preserved in the normal way.

The dissociation in these perceptions — and the literature proves that it has been observed more than once — is most remarkable. It shows that the conduction of pain- and heat-sensation within the entire region of the trigeminus ought necessarily to be sought for in the tractus spinalis of this nerve, which has been interrupted in the proximal oblongata. The tactile impressions may still find their way along the nucleus sensibilis N. V, which remains unimpaired (as are likewise the N. motorius and its radix mesencephalicus). It is interesting that the reflex-action of the cornea has disappeared and that the cornea no longer perceives anything. Probably the cornea — without tactile corpuscles and without hairs — does not possess any contrivance for the tactile sense.

The interruption of the spino-thalamic tract on the left side is assumed to be responsible for the defective conduction of the thermal and pain-stimuli in the right half of the body.

The lemniscus medialis, is not attained by the lesion — the long

posterior root-fibres end in the nuclei of GOLL and BURDACH, and the fibres originating in these nuclei have continued their course therein through the decussatio lemnisci — from this is determined the intactness of deep sensibility (stereognosia, sense of space, perception of passive and active motion of the right half of the body).

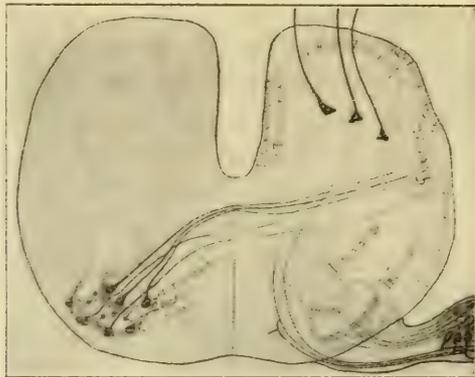
It is generally taken for granted that the thin fibres in the marginal zone of LISSAUER conduct their impulses into the fibres of the spongiosa of the formatio ROLANDO, and after passing through the substantia gelatinosa and the cells of GIERKE are absorbed by the *terminal* cells, adjacent to the substantia gelatinosa.

The axones of the cells are then thought to cross one another in the anterior (and posterior) commissure, and to continue their course as tractus spino-thalamicus in the lateral column of the medulla.

It is just because of experiences similar to the case here described that the tractus spinothalamicus has been assumed to be invested with the function of conducting the thermal and pain-impulses.

It is different for the tactile sense. Tactile impulses enter likewise into the thin fibres of the zone of LISSAUER, but they may pass thence immediately into the marginal cells of the spongiosa of the formatio ROLANDO, — the zonal cells. Their axones may ascend as well through the posterior as through the lateral cords of the unilateral and the contralateral side, it is even most probable that these prolongations are so diffused in the tegmentum of the spinal cord, that the conduct of these impulses remains possible as long as even a small part of it has been preserved. In the left half of the

Fig. IV. Scheme of the LISSAUER marginal zone and of the substantia ROLANDO with the origin of the tractus spino-thalamicus.



oblongata there is a sufficient number of fibres, both in the lemniscus medialis and in the median portions of the formatio reticularis grisea

to bring about the conduct of the tactile impressions from the right half of the body. The tactile sense of the right side remains therefore undisturbed.

II. The paralysis of the swallowing muscles to the left (that has been much meliorated) and the lasting paralysis of the muscles of the larynx on that side are symptoms following almost necessarily from the former. The ventral (motor) nucleus of the IX<sup>th</sup>, X<sup>th</sup> and XI<sup>th</sup> nerve has been destroyed by the lesion.

Whether the dorsal vagus nucleus has been injured, forms an independent question. For the moment the sense of taste to the left has suffered only very slightly. Those who believe the tractus solitarius to be a continuation of centripetal glosso-pharyngeus-fibres — as it doubtlessly is in part — and who consider it as a tract conducting taste-impulses, will be rather inclined to think it has not been injured.

On the other hand the analgesia transgresses into the zone of the N. trigeminus in the region of the ear, whilst pain- and heat-sensation are disturbed in the dermal branch dependent on the N. X, a fact easily to be understood, considering the destroying of the forthcoming roots of this nerve.

III. The dissociation of the conjugate movement of the eyes and the head towards the right.

I believe this symptom to be a consequence of the portio interna corporis restiformis to the left. Within this portion is contained the radix descendens N. VIII. It contains the descending root-fibres of the N. vestibularis, which enter into it on a higher plane than that where is situated the focus of disease. The N. vestibularis herefore has been destroyed partially, not completely — the coldwater-reaction of BARANY proves that vestibularis-impulses still act upon the double-eye.

The influence of the one-sided destruction of the vestibular tonus on the double-eye is well-known. Both in man and in animals the uni-lateral eye is turned downward and inward, the contro-lateral one upward and outward. They deviate therefore in a direction opposite to the lesion.

In the present case however that involuntary stand of the eyes has found compensations, amongst others the oblique attitude of the head. The motor mechanism for the double eye is consequently brought into another state of equilibrium than the normal one. It undergoes an innervation tendency to direct both eyes more than is usual towards the left side.

This mechanism has been disposed in that way by means of reflex-actions through the exercise that has led to compensation.

As soon as a voluntary act does make use of the motor mechanism of the double eye which is connected indissolubly with the turning of the head towards the right, there will necessarily be made an endeavour to employ another mechanism than that existing in the normal.

The prevailing innervation-tendency for turning the eyes towards the left is now in conflict with the impulse of turning towards the right. As a result of it, first the turning of both eyes towards the left may be observed, whilst it is only after this that the position of extreme turning towards the right is attained.

As a consequence of this the fixation of the eyes on objects standing to the right is not synchronic with the turning of the head. Therefore these objects are not instantly recognized, as long as the settling of the eyes remains defective.

The same case does present itself if the head is turned towards the left, with this difference that no turning of the double eye towards the left then precedes. In this latter case the voluntary and the reflective movements are added up together, the eyes are moving too quickly, with the result that objects standing on the right are again not instantly well-recognized, though the irregularity is redressed much sooner than when looking towards the right. As fourth and last symptom we find the static ataxy shown by the patient, a symptom that may depend either on an interruption of rubro-spinal or vestibulo-spinal tracts, or on the softening that probably exists at the base of the cerebellum, or on both.

All symptoms taken together however indicate a sudden inefficacy of the nerve-area, irrigated by the arteria cerebelli posterior inferior.

**Chemistry.** — “*The metastability of the Metals in consequence of Allotropy and its significance for Chemistry, Physics and Technics. III.*” By Prof. ERNST COHEN and G. DE BRUIN.

*The specific Heat of the Metals 2.*

1. In the first paper on this subject<sup>1)</sup> it was pointed out that the existing data on the physical and mechanical constants of metals known up to the present are to be considered as entirely fortuitous values, since they refer to the indefinite metastable systems which are produced when metals pass from the molten to the solid state. In other words: all physical and mechanical constants of the metals are functions of the previous thermal history of the specimen experimented with.

<sup>1)</sup> Proc. 16, 632 (1913).

In the second paper <sup>1)</sup> we called attention to the fact that this result was corroborated by LE VERRIER's experiments, who found as long as twenty two years ago, that the specific heat of Pb, Zn, Al, Ag, and Cu is a function of the previous thermal treatment of these metals.

2. Although the values given by LE VERRIER are mentioned in different physico-chemical tables, only small attention has been given to them. In those cases where this has been done, they have generally been considered as less accurate. Such is for example the case with SCHÜBEL <sup>2)</sup>, who says in a paper published recently :

“Nicht mit aufgenommen sind die Beobachtungen von LE VERRIER, Al, Cu, Ag, Zn; LE VERRIER findet Unstetigkeiten in seinen Kurven der mittleren spezifischen Wärme als Funktion der Temperatur, welche nicht wieder beobachtet wurden, so dass die von ihm gefundenen Werte für die mittlere spezifische Wärme höchst unwahrscheinlich geworden sind.”

3. However, it may be pointed out that others would have been able to find the same results as LE VERRIER only if they had investigated specimens of the same metal possessing different thermal histories, as LE VERRIER did.

We shall see below what discrepancies occur if this precaution is omitted. It will be proved then also that LE VERRIER has been up to the present the only investigator who has paid sufficient attention to this point.

4. The fact that different authors have found (at the same temperature) for a certain metal very different values of the specific heat, must partly be attributed to their omitting to take into account the previous heat treatment of the metal experimented with. From the enormous material found in the literature, we only quote here the values for bismuth found at 18° by L. LORENZ <sup>3)</sup> to be 0,0303, whilst JAEGER and DIESSELHORST <sup>4)</sup> give 0,0292. The difference is 3 percent. But also differences as high as 13 percent occur, as might be seen from the paper of SCHÜBEL; mentioned above.

5. That these facts recently have attracted notice on the part of

<sup>1)</sup> Proc. 17, 200 (1914).

<sup>2)</sup> Zeitschr. f. anorg. Chemie 87, 81 (1914).

<sup>3)</sup> Wied. Ann. 13, 437 (1881).

<sup>4)</sup> Abhandl. der Physik. Techn. Reichsanstalt 3, 269 (1900).

physicists, is evident from a paper published by E. H. GRIFFITHS and EZER GRIFFITHS <sup>1)</sup>, who say: "a further possible source of uncertainty is the effect of sudden chilling of a metal when rapidly cooled from a high temperature. However they do not mention the reasons which led them to this conclusion.

As these investigations as well as those of EZER GRIFFITHS <sup>2)</sup> on "The variation with temperature of the specific Heat of Sodium in the Solid and Liquid State", play an important rôle in our subsequent arguments, we must dwell upon them.

Using a special calorimeter in which the metal was electrically heated, they determined the *true* specific heat of different metals (Cu, Ag, Zn, Sn, Pb, Al and Cd <sup>3)</sup>) at different temperatures. As the substances were raised from a given temperature through very small ranges of temperature (about 1.4° C.) their previous thermal history was not changed by the experiment itself. Evidently this is of high importance, as in the methods in use up to the present (method of mixtures, ice-calorimeter) the substances are heated to considerably higher temperatures by which procedure changes may occur which are uncontrollable.

6. The metals experimented with were of high purity. In this way Messrs. GRIFFITHS succeeded in determining for a certain piece of metal at a definite temperature values of the specific heat which were quite *reproducible* while the conditions of the experiments were changed within wide limits. For a certain piece of copper, the previous thermal history of which was however indefinite, they found at 0° C.:

Mean of 5 independent determinations 0.09094 (probable experimental error of the group 0.01 percent).

Mean of 5 independent determinations 0.09079 (probable experimental error of the group 0.03 percent).

Mean of 4 independent determinations 0.09098 (probable experimental error of the group 0.05 percent).

Mean of 4 independent determinations 0.09088 (probable experimental error of the group 0.08 percent).

7. The metals used by the authors were *cast*. Evidently they were of opinion that the condition of their material was definite. This is most surprising, as they themselves called attention to the

<sup>1)</sup> Phil. Trans. Roy. Soc. London **213** (A), 119 (1914).

<sup>2)</sup> Proc. Roy. Soc. London **89**, (A) 561 (1914).

<sup>3)</sup> And Iron.

fact that previous thermal treatment must be taken into account. It will be proved below that the metals experimented with by MESSRS. GRIFFITHS did not correspond to definite states: the values they found for the specific heat must therefore be considered as *fortuitous* values. This is the more to be regretted as their measurements were carried out with the greatest care.

8. We shall now consider the experiments concerning sodium.

The high importance of this research with respect to the question which occupies us, may be characterized by the following four points:

*a.* The previous thermal history of the pure metal was strictly defined.

*b.* Each value given for the *true* specific heat is the mean of 4 or 6 independent determinations which were carried out under varying conditions (change of the quantity of electric energy supplied). As the tables (I and II) show, the agreement of the measurements is perfect.

*c.* The determinations have been carried out with the *solid* metal from  $0^{\circ}$  up to the melting point.

*d.* The authors have exclusively taken the standpoint of experimental physicists, giving their quantitative results without any commentary.

9. Concerning the item *a* the following may be pointed out. The authors had found that the true specific heat of *molten* sodium can be reproduced with great accuracy, even if the previous heat treatment of the molten metal is changed within wide limits. The contrary occurs with the *solid* metal: discrepancies of 2 per cent at the same temperature were found in their early experiments. Referring to this result they say: "The importance of this point was not sufficiently realised in the early determinations and a large number of otherwise excellent experiments have been rendered worthless through lack of attention to the precise nature of the previous heat-treatment."

The metal used in the final experiments was prepared as follows:

"*Annealed*". (Table I): The rate of cooling from the liquid state was less than  $4^{\circ}$  per hour, which was the rate of fall of the bath from  $100^{\circ}$  to  $86^{\circ}$ .

"*Quenched*". (Table II): The metal was heated in an oil bath to  $130^{\circ}$  and then rapidly transferred to a vessel of ice-cold water.

The metal was enclosed in a case of copper of special form. The determinations with the quenched metal were made starting from the lowest temperature ( $0^{\circ}$  C.) and progressing in steps up to  $95^{\circ}$ .

TABLE I.  
Na — slowly cooled (Annealed)

Temperature	Data	Spec. Heat	Mean
0°	Aug. 28	0.2835 0.2836 0.2820 0.2826	0.2829
28°.82	Aug. 19	0.2911 0.2910 0.2929 0.2893	0.2910
49°.38	Aug. 8	0.2954 0.2952 0.2951 0.2955 0.2951 0.2955	0.2953
49°.27	Aug. 16	0.2946 0.2949 0.2964	0.2953
49°.07	Aug. 17 Aug. 20	0.2963 0.2945 0.2942	0.2950
67°.79	Aug. 21	0.3014 0.3037 0.3018 0.3010 0.3018	0.3019
79°.15	Aug. 22	0.3083 0.3085 0.3086 0.3079	0.3083
85°.65	Aug. 15	0.3168 0.3181 0.3165 0.3178 0.3159	0.3171
90°.03	Aug. 23	0.3209 0.3208 0.3208 0.3210	0.3209
95°.53	Aug. 24	0.3260 0.3254 0.3260	0.3258

If the cooling had taken place very slowly, the values found at each temperature were definite and reproducible. This proves that the values given in table I refer to the *state of equilibrium* at the

TABLE II.  
Na — "quenched".

Temperature	Data	Spec. Heat	Mean
0°	Aug. 29	0.2892 0.2874 0.2864 0.2852	<b>0.2870</b>
40°.16	Aug. 30	0.2973 0.3002 0.2953 0.2992 0.2983	<b>0.2981</b>
68°.60	Aug. 31	0.3024 0.3049 0.3073	<b>0.3040</b>
68°.60	Sept. 2	0.3034 0.3020 0.3038	
82°.15	Sept. 3	0.3087 0.3094 0.3095 0.3079	<b>0.3089</b>
94°.02	Sept. 4	0.3195 0.3213 0.3192 0.3200	<b>0.3200</b>

corresponding temperature. The measurements of 8 Aug. giving the value 0.2953 (at 49°.38) having been completed, the metal was taken out of the calorimeter, heated up to 100° (melted) and allowed to cool *rapidly* in air. The value then obtained for the specific heat (at 49°.38) was 0.3014. Again heating to 100° (melting) and allowing to cool *very slowly*, gave the value 0.2953 (at 49°.38), identical with the value previously obtained for the "annealed" metal. Evidently the process is a *reversible* one.

10. We shall now consider the diagram (fig. 1 See next p. 932) which represents the results graphically. The broken line *apb* represents the results of the determinations after the sodium had had been quenched whilst the curve *cpd* represents those concerning the solid metal. This diagram is also given by EZER GRIFFITHS without any commentary.

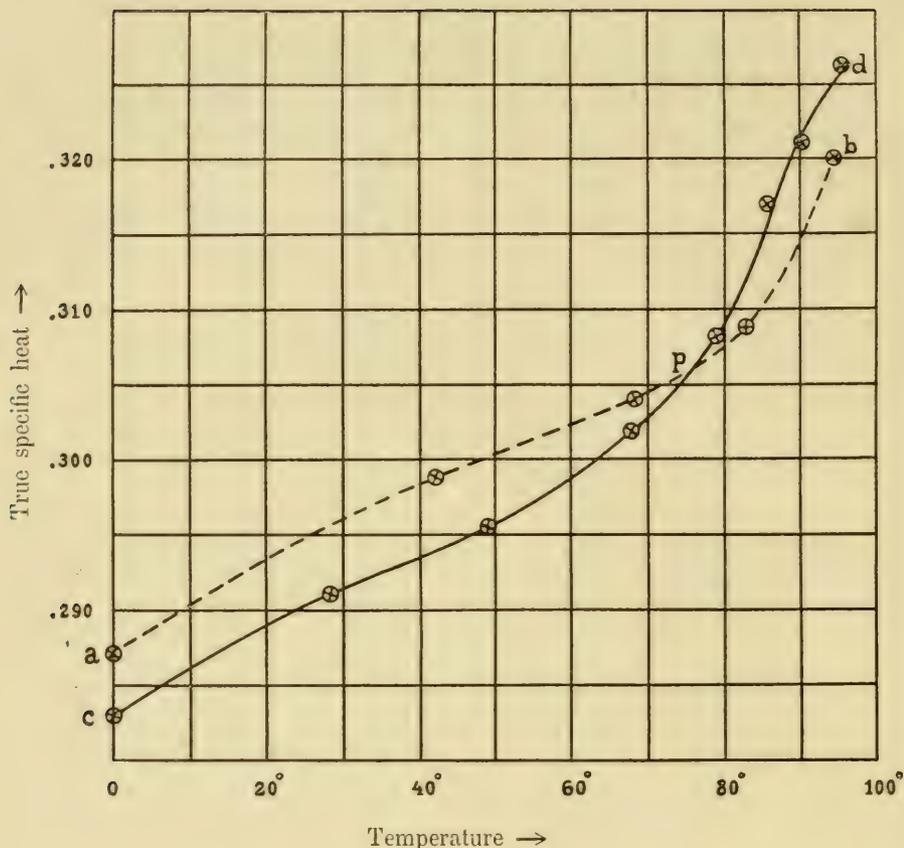


Fig. 1.

Considering the figure more closely it is evident that sodium has a transition point between  $0^\circ$  and  $90^\circ$ : this was not known up to the present <sup>1)</sup>.

11. We have here for the first time a case where it is possible to obtain at will, and in nearly quantitative yield, either the stable or the metastable solid modification from a metallic melt. Until now ERNST COHEN, HELDERMAN, MOESVELD and VAN DEN BOSCH have not been able to get this result in their investigations on bismuth <sup>2)</sup>, copper <sup>3)</sup>, zinc <sup>4)</sup>, antimony <sup>5)</sup> and lead <sup>6)</sup>. In these cases the different modi-

<sup>1)</sup> SCHÄDLER [Lieb. Ann. **20**, 2 (1836)], thinks it probable that sodium crystallizes in the regular system, whilst LONG [Journ. Chem. Soc. **13**, 122 (1860)] found that it is also able to crystallize in the quadratic system.

<sup>2)</sup> Zeitschr. f. physik. Chemie **85**, 419 (1913).

<sup>3)</sup> Proc. **16**, 628 (1913); **17**, 60 (1914).

<sup>4)</sup> Proc. **16**, 565 (1913); **17**, 59, 641 (1914).

<sup>5)</sup> Proc. **17**, 645 (1914).

<sup>6)</sup> Proc. **17**, 822 (1914).

fications were always simultaneously present in the material experimented with.

Only with cadmium<sup>1)</sup> did they succeed in preparing the pure  $\alpha$ ,  $\beta$  and  $\gamma$ -modifications by preparing electrolytically the  $\gamma$ -form, which was transformed afterwards into the  $\beta$ - or  $\alpha$ -modification.

12. From the work of COHEN and his collaborators it follows that a piece of sodium, chosen at random, is at ordinary temperatures in a metastable condition, as there are simultaneously present both the  $\alpha$ - and  $\beta$ -sodium. This conclusion is proved in a quantitative way by the very exact measurements of EZER GRIFFITHS. It is to be expected that sodium which has received heat treatment of an intermediate character (between chilling and annealing) will have at a given temperature a specific heat between the values found at the same temperature for the "chilled" and "annealed" material respectively.

The following experiment proves that this is really the case. The metal was melted and allowed to cool freely in air. (Samples *A* and *B*, table III). Whilst the specific heat of the "annealed" metal was found to be 0.2829 at 0° C. and that of the chilled 0.2870, the experiment gave now (at 0° C.) the values of table III.

The specific heat values are found now between 0.2829 and 0.2870.

GRIFFITHS says: "Several determinations were made at temperatures between 88° and 94° after a somewhat similar heat-treatment, and the same feature is common to all, the values falling between the extremes corresponding to the "annealed" and the "quenched" states".

TABLE III.

Preparation	Date	Spec. heat at 0° C.	Mean
<i>A</i>	April 7	0.2861	<b>0.2864</b>
		0.2868	
		0.2866	
		0.2864	
		0.2858	
<i>B</i>	June 4	0.2864	<b>0.2863</b>
		0.2871	
	" 5	0.2862	
		0.2855	
	" 6	0.2864	
		0.2863	

<sup>1)</sup> Proc. 16, 485 (1913); 17, 54, 122, 638 (1914).

13. These experiments consequently prove in a quantitative way that sodium as it has been known up to the present, is also a metastable system in consequence of allotropy and that the physical and mechanical constants of this metal which have been determined hitherto (except the values of the specific heat, mentioned in the tables I and II) are entirely fortuitous values.

14. Some preliminary experiments carried out by EZER GRIFFITHS proved that there exists a measurable difference between the densities of  $\alpha$ - and  $\beta$ -sodium at the same temperature. We hope to report shortly on some dilatometric measurements in this direction.

### *Summary of Results.*

Relying on the investigations of ERNST COHEN, HELDERMAN, MOESVELD and VAN DEN BOSCH and those of E. H. and EZER GRIFFITHS on the true specific heat of metals at different temperatures we find that:

1. The true specific heat of sodium is a function of its previous thermal history.

2. Both with the slowly cooled and the chilled metal, at a definite temperature definite and reproducible values of this physical constant are found.

3. An intermediate previous thermal history gives values of the specific heat between the extremes mentioned under 2.

4. The experiments of LE VERRIER (1892) on the specific heat of metals which had not been understood up to the present are corroborated by the investigations recently carried out with high precision by E. H. and EZER GRIFFITHS.

5. Sodium is enantiotropic; there exists a transition temperature between  $0^{\circ}$  and  $90^{\circ}$  C. <sup>1)</sup>

6. Sodium, as it is known hitherto, is a metastable system as might be expected on account of the investigations on bismuth, cadmium, copper, zinc, antimony and lead, described some time ago.

7. All physical and mechanical "constants" known up to the present of the metals are entirely fortuitous values; they must be redetermined with the pure  $\alpha$ -,  $\beta$ -,  $\gamma$ -, . . . modifications of these substances.

*Utrecht*, December 1914.

VAN 'T HOFF-*Laboratory*.

<sup>1)</sup> The exact position of this point will be determined by dilatometric measurements.

**Mathematics.** — “Characteristic numbers for nets of algebraic curves.” By PROFESSOR JAN DE VRIES.

(Communicated in the meeting of November 28, 1914).

1. The curves of order  $n$ ,  $c^n$ , which belong to a net  $N$ , cut a straight line  $l$  in the groups of an involution of the second rank,  $I_n^2$ . The latter has  $3(n-2)$  groups each with a triple element<sup>1</sup>);  $l$  is therefore stationary tangent for  $3(n-2)$  curves of  $N$ .

Any point  $P$  is base-point of a pencil belonging to  $N$ , hence inflectional point for three curves<sup>2</sup>) of  $N$ .

The locus of the inflectional points of  $N$  which send their tangent  $i$  through  $P$ , is therefore a curve  $(I)_P$  of order  $3(n-1)$  with triple point  $P$ .

If the net has a base-point in  $B$  any straight line through  $B$  is stationary tangent with point of inflection in  $B$ . Consequently  $(I)_P$  passes through all the base-points of the net.

We shall suppose that  $N$  has only single base-points.

On  $PB$   $N$  determines an  $I_{n-1}^2$ ; the latter has  $3(n-3)$  triple elements; from which it ensues that  $B$  is an inflectional point of  $(I)_P$  having  $PB$  as tangent  $i$ .

Through  $P$  pass  $3(n-1)(2n-3)$  straight lines, each of which touch a singular curve in its node<sup>3</sup>); all these nodes  $D$  lie apparently on  $(I)_P$ .

2. Every  $c^n$ , which osculates  $l$  in a point  $I$ , cuts it moreover in  $(n-3)$  points  $S$ . We consider the locus of the points  $S$ , which belong in this way to  $(I)_P$ . Since  $P$ , as base-point of a pencil, lies on  $3(n-3)(n+1)$  tangents of inflexion<sup>4</sup>), the curve  $(S)$  has in  $P$  a  $3(n-3)(n+1)$ -fold point. Apart from  $P$  each ray of the pencil  $(P)$  contains  $3(n-2)(n-3)$  points  $S$ ; hence  $(S)$  is a curve of order  $3(n-3)(2n-1)$ .

Let us now consider the correspondence between the rays  $s$  and  $s'$ , which connect a point  $M$  with two points  $S$  and  $I$  belonging to

1) If the  $I_n^2$  is transported to a rational curve  $c^n$  and determined by the field of rays, these groups lie on the stationary tangents.

2) For the characteristic numbers of a pencil my paper “Faisceaux de courbes planes” may be referred to (Archives Teyler, sér. II, t. XI, 99—113). For the sake of brevity it will be quoted by  $T$ .

3) Cf. for instance my paper “On nets of algebraic plane curves”. (Proceedings volume VII, p. 631).

4)  $T$ . p. 100.

the same  $c^n$ . Any ray  $s$  contains  $3(n-3)(2n-1)$  points  $S$ , determines therefore as many rays  $s'$ ; any ray  $s'$  contains  $3(n-1)$  points  $I$ , determines therefore  $3(n-1)(n-3)$  points  $S$  and consequently as many rays  $s$ . The number of rays of coincidence  $s' \equiv s$  amounts therefore to  $3(n-3)(2n-1) + 3(n-3)(n-1) = 3(n-3)(3n-2)$ . The ray  $MP$  contains  $3(n-2)$  points  $I$ , which are each associated to  $(n-3)$  points  $S$ ; consequently  $MP$  represents  $3(n-2)(n-3)$  coincidences. The remaining  $6n(n-3)$  coincidences arise from coincidences  $I \equiv S$ , consequently from *points of undulation*  $U$ . Through  $P$  pass consequently  $6n(n-3)$  *four-point tangents*  $t_4$ ; the tangents  $t_4$  envelop therefore a curve of class  $6n(n-3)$ .

3. We further consider the correspondence between the rays  $s_1, s_2$ , which connect  $M$  with two points  $S$  belonging to the same point  $I$ . This symmetrical correspondence has apparently as characteristic number  $3(n-3)(2n-1)(n-4)$ . The ray  $MP$  contains  $3(n-2)$  points of inflection, hence  $3(n-2)(n-3)(n-4)$  pairs  $S_1, S_2$ ; as many coincidences  $s_1 \equiv s_2$  coincide with  $MP$ . The remaining coincidences pass through points of contact of tangents  $t_{2,3}$  (straight lines, which touch a  $c^n$  in a point  $R$  and osculate it in a point  $I$ ). The tangents  $t_{2,3}$  envelop therefore a curve of class  $9n(n-3)(n-4)$ .

4. Let  $a$  be an arbitrary straight line; each of its points is, as base-point of a pencil, point of inflection for three  $c^n$ . The curves  $c^n$  coupled by this to  $a$  form a system  $[c^n]$  with index  $6(n-1)$ ; for the inflectional points of the curves  $c^n$ , which pass through a point  $P$ , lie on a curve of order  $6(n-1)^1$ , and the latter cuts  $a$  in  $6(n-1)$  points  $I$ . The stationary tangents  $i$ , which have their point of contact  $I$  on  $a$ , form a system  $[i]$  with index  $3(n-1)$ , for through a point  $P$  pass the straight lines  $i$ , which connect  $P$  with the intersections of  $a$  and  $(I)_P$ .

The systems  $[c^n]$  and  $[i]$  are projective; on a straight line  $l$  they determine between two series of points a correspondence which has as characteristic numbers  $6(n-1)$  and  $3(n-1)n$ . The coincidences of this correspondence lie in the points, in which  $l$  is cut by the loci of the points  $I$  and  $S$ , which every  $i$  determines on the associated  $c^n$ . As any point of  $a$  is point of inflection for three  $c^n$ ,  $a$  belongs nine times to the locus in question. Hence the points  $S$  lie on a curve  $(S)_a$  of order  $3(n^2+n-5)$ .

For  $n=3$  the number 21 is found; this is in keeping with the

<sup>1)</sup> T. p. 104.

well-known theorem, according to which a net of cubics contains 21 figures, composed of a conic and a straight line.

5. To the intersections of  $a$  with the curve  $(S)_a$  belong the  $3(n-2)$  groups of  $(n-3)$  points  $S$ , arising from the curves  $c^n$ , which osculate  $a$ . In each of the remaining  $3(n^2+n-5) - 3(n-2)(n-3)$  intersections a point  $I$  coincides with a point  $S$  of one of the three  $c^n$ , which have  $I$  as point of inflection. The corresponding tangent  $i$  then has in common with  $c^n$  four points coinciding in  $I$ , so that  $I$  is point of undulation. *The points of undulation of the net lie therefore on a curve  $(U)$  of order  $3(6n-11)$ .*

For  $n=3$  we find the 21 straight lines belonging to the degenerate cubics of the net.

As a base-point  $B$  of a net is point of inflection of  $\infty^1$  curves  $c^n$ , there will have to be a finite number of curves, for which  $B$  is point of undulation. In order to find this number we consider the locus of the points  $T$  which any ray  $t$  passing through  $B$  has still in common with the  $c^n$ , which osculates it in  $B$ . As  $B$  is point of inflection on three  $c^n$  of the pencil which has an arbitrary point  $P$  as base-point, the curves of  $N$  falling under consideration here form a system  $[c^n]$  with index three, which is projective with the pencil of rays  $(t)$ .

The two systems produce a curve of order  $(n+3)$ , which is cut by a ray  $t$  in  $(n-3)$  points  $T$ . Consequently it has in  $B$  a sextuple point, and there are six curves  $c^n$ , on which  $B$  is point of undulation.

If the net has *base-points* they are *sixfold points* on the curve  $(U)$ .

For  $n=3$  the curve degenerates into a sixray, which consists of parts of compound curves.

6. To each  $c^n$ , which possesses a point of undulation  $U$  we shall associate its fourpoint tangent  $u$ ; the latter cuts it moreover in  $(n-4)$  points  $V$ . The locus of the points forms with the curve  $(U)$  counted four times the product of the projective systems  $[c^n]$  and  $[u]$ . In the pencil which a point  $P$  sets apart from  $N$  occur  $6(n-3)(3n-2)$  curves, which possess a point  $U^1$ ; this number is therefore the index of  $[c^n]$ . The system  $[u]$  has, as appears from § 2, the index  $6n(n-3)$ . In a similar way as above (§ 4) we find now for the order of  $(V)$   $6(n-3)(3n-2) + 6n^2(n-3) - 12(6n-11) = 6(n-4)(n^2+4n-7)$ .

We now associate on each straight line  $u$  the point  $U$  to each

<sup>1)</sup> T. p. 105.

of the  $(n-4)$  points  $V$ . By this the rays of a pencil ( $M$ ) are arranged into a correspondence with characteristic numbers  $3(6n-11)(n-4)$  and  $6(n-4)(n^2+4n-7)$ . Observing that the  $6n(n-3)$  fourpoint tangents, which meet in  $M$ , represent  $(n-4)$  coincidences each, we find for the coincidences  $U \equiv V$  the number

$(n-4) [3(6n-11) + 6(n^2+4n-7) - 6n(n-3)] = 15(n-4)(4n-5)$ . This is therefore the *number of curves  $c^n$  with a fivepoint tangent  $t_5$* .

Let us now consider the correspondence between two points  $V_1, V_2$ , which lie on the same tangent  $u$ . Using the correspondence arising between the rays  $MV_1, MV_2$  we find in a similar way for the number of coincidences  $V_1 \equiv V_2$   $12(n^2+4n-7)(n-4)(n-5) - 6n(n-3)(n-4)(n-5) = 6(n-4)(n-5)(n^2+11n-14)$ . With this the *number of curves of  $N$  has been found, which are in possession of a tangent  $t_{4,2}$ , consequently of a point of undulation, the tangent of which touches the curve moreover.*

**7.** The involution of the second rank, which  $N$  determines on a straight line  $l$ , has  $2(n-2)(n-3)$  groups, each of which possesses two double elements;  $l$  is therefore bitangent for as many curves of the net. If  $l$  rotates round a point  $P$ , the points of contact  $R, R'$  will describe a curve, which passes  $(n-3)(n+4)$  times through  $P$ ; for  $P$  as base-point of a net lies on  $(n-3)(n+4)$  curves, which are each touched in  $P$  by one of their bitangents. From this follows that the locus of the pairs  $R, R'$ , which we shall indicate by  $(R)_P$  is a curve of order  $(n-3)(5n-4)$ .

If we consider the correspondence  $(R, R')$  on the rays of the pencil ( $P$ ), and, in connection with this, the correspondence between the rays  $MR, MR'$ , we arrive at the number of coincidences  $R \equiv R'$  and we find once more that the fourpoint tangents envelop a curve of class  $6n(n-3)$ .

Let us now determine the order of the locus of the groups of  $(n-4)$  points  $S$ , which  $l$  has in common with the  $2(n-2)(n-3)$  curves  $c^n$ , for which  $l$  is bitangent. The pencil determined by  $P$  contains  $2(n-3)(n-4)(n+1)$  curves which are cut<sup>1)</sup> in  $P$  by one of their bitangents. This number indicates at the same time the number of branches of the curve  $(S)_P$  passing through  $P$ ; for its order we find therefore  $2(n-3)(n-4)(n+1) + 2(n-2)(n-3)(n-4)$ , or  $2(n-3)(n-4)(2n-1)$ .

If we associate each point  $R$  to each of the points  $S$  belonging to the same  $c^n$ , a correspondence is determined in the pencil of rays

<sup>1)</sup> T. p. 102.

with vertex  $M$ , which correspondence has  $(n-3)(5n-4)(n-4)$  and  $4(n-3)(n-4)(2n-1)$  as characteristic numbers.

Since the ray  $MP$  contains  $4(n-2)(n-3)$  points  $R$ , which are each associated to  $(n-4)$  points  $S$ , so that  $MP$  is to be considered as  $4(n-2)(n-3)(n-4)$ -fold coincidence, we find for the number of coincidences  $9n(n-3)(n-4)$ . By this we again find the class of the curve enveloped by the tangents  $t_{2,3}$  (cf. § 3).

A new result is arrived at from the correspondence between two points  $S_1, S_2$  belonging to the same pair  $R, R'$ . The symmetrical correspondence between the rays  $MS_1, MS_2$  has as characteristic number  $2(2n-1)(n-3)(n-4)(n-5)$ . Any of the groups of  $(n-4)$  points  $S$  lying on  $MP$  produces  $(n-4)(n-5)$  pairs  $S_1, S_2$ , so that  $MP$  represents  $2(n-2)(n-3)(n-4)(n-5)$  coincidences. The remaining  $[4(2n-1) - 2(n-2)](n-3)(n-4)(n-5)$  coincidences are, taken three by three, points of contact of triple tangents  $t_{2,2,2}$ . *Through an arbitrary point  $P$  pass consequently  $2n(n-3)(n-4)(n-5)$  triple tangents.*

**8.** Let  $a$  again be an arbitrary straight line; each of its points is, as base-point of a pencil belonging to  $N$ , point of contact  $R$  of  $(n+4)(n-3)$  bitangents  $d^1$ ). We determine the order of the locus of the second point of contact  $R'$ . The latter has in common with  $a$  the pairs of points  $R, R'$ , in which  $a$  is touched by  $c^n$ , and also the points of undulation ( $R' = R$ ), lying on  $a$ , consequently  $4(n-2)(n-3) + 3(6n-11)$  or  $(4n^2 - 2n - 9)$  in all. This number is apparently the order of the curve  $(R')_n$  in question.

In order to determine the locus of the points  $W$ , which each bitangent  $d$  of the system in question has moreover in common with the  $c^n$ , twice touched by it, we associate to each of those curves  $c^n$ , the bitangent  $d$ , for which the point of contact  $R$  lies on  $a$ .

To the pencil, which a point  $P$  sets apart from  $N$ , a curve of order  $(n-3)(2n^2 + 5n - 6)$  is associated, which contains the points of contact of the bitangents to the curves of that pencil<sup>2)</sup>. By this the number of straight lines  $d$  becomes known, of which a point of contact lies on  $a$ ; the system  $[c^n]$  has therefore as index  $(n-3)(2n^2 + 5n - 6)$ . The index of the system  $[d]$  is  $(n-3)(5n-4)$ ; for this is (§ 7) the number of intersections of  $a$  with the curve  $(R)_P$ . The systems  $[c^n]$  and  $[d]$  rendered projective, produce a locus of order  $(n-3)(2n^2 + 5n - 6) + n(n-3)(5n-4)$ . To it belongs the straight

<sup>1)</sup> T. p. 102.

<sup>2)</sup> Bitangential curve; cf. T. p. 107.

line  $a$   $2(n+4)(n-3)$ -times, because each of its points is point of contact of  $(n+4)(n-3)$  bitangents. The curve  $(R')_a$  belongs moreover twice to it. For the order of the curve  $(W)_a$  we find consequently  $(n-3)(7n^2+n-6)-2(n-3)(n+4)-2(4n^2-2n-9)=(n-4)(7n^2-2n-15)$ .

We now consider the correspondence between the rays  $r' = MR'$  and  $w = MW$ . A ray  $r'$  contains  $(4n^2-2n-9)$  points  $R'$ , consequently determines  $(4n^2-2n-9)(n-4)$  rays  $w$ ; to a ray  $w$   $(n-4)(7n^2-2n-15)$  rays  $r'$  are associated. Each of the  $(n-3)(5n-4)$  lines  $d$ , which connect  $M$  with the intersections of  $a$  and  $(R)_M$ , is apparently an  $(n-4)$ -fold coincidence. The number of coincidences  $R' \equiv W$  amounts therefore to  $(n-4)[(4n^2-2n-9) + (7n^2-2n-15) - (n-3)(5n-4)] = (n-4)(6n^2+15n-36)$ . This number is the order of the locus  $(R)_{2,3}$  of the points of contact  $R$  of the tangents  $t_{2,3}$ .

9. In order to find also the order of the locus  $(I)_{2,3}$  of the inflectional points  $I$  of the tangents  $t_{2,3}$ , we return to the system  $[c^n]$  considered in § 4, of which all the curves have an inflectional point  $I$  on a given line  $a$ . The points  $S$ , which the corresponding stationary tangent has moreover in common with  $c^n$ , lie on a curve  $(S)_a$  of order  $3(n^2+n-5)$ . We consider now the correspondence between two points  $S_1, S_2$  of the same curve. It determines in a pencil of rays  $(M)$  a symmetrical correspondence with characteristic number  $3(n^2+n-5)(n-4)$ . The rays connecting  $M$  with the intersections of  $a$  and  $(I)_M$ , are  $(n-3)(n-4)$ -fold coincidences; as their number amounts to  $3(n-1)$  (§ 1), we find for the number of coincidences  $S_1 \equiv S_2$   $[2(n^2+n-5) - (n-1)(n-3)]$  or  $3(n-4)(n^2+6n-13)$ . This, however, is also the number of tangents  $t_{2,3}$ , the point of inflection of which lies on  $a$ , consequently the order of the locus  $I_{2,3}$  of the points of inflection of the tangents  $t_{2,3}$ .

By means of the curves  $(R)_{2,3}$  and  $(I)_{2,3}$ , belonging to the system  $[t_{2,3}]$ , we can again determine the number of fivepoint-tangents  $t_5$ . For this purpose we associate the lines  $MR$  and  $MI$ , on account of which a correspondence with characteristic numbers  $3(n-4)(2n^2+5n-12)$  and  $3(n-4)(n^2+6n-13)$  arises. The  $9n(n-3)(n-4)$  tangents  $t_{2,3}$  converging in  $M$  are coincidences. On the remaining ones  $R$  coincides with  $I$ . So we find for the number of the  $t_5$   $3(n-4)(3n^2+11n-25) - 9n(n-3)(n-4)$  or  $15(n-4)(4n-5)$ .

10. We return to the system  $[c^n]$  of the curves, which (§ 8) are each touched by one of their bitangents  $d$  in a point  $R$  of a straight line  $a$ .

If on a line  $d$  two of the points  $W$  coincide  $d$  becomes a triple

tangent. The correspondence between two points  $W_1, W_2$  of a same  $c^n$  determines in the pencil of rays  $M$  a symmetrical correspondence with characteristic number  $(7n^2 - 2n - 15)(n - 4)(n - 5)$ . As each bitangent through  $M$  having one of its points of contact on  $a$ , represents  $(n - 4)(n - 5)$  coincidences, the number of coincidences  $W_1 \equiv W_2$  amounts to  $2(n - 4)(n - 5)(7n^2 - 2n - 15) - (n - 4)(n - 5)(n - 3)(5n - 4) = (n - 4)(n - 5)(9n^2 + 15n - 42)$ . As they lie two by two on tangents  $t_{2,2,2}$ , the locus of the points of contact of the triple tangents is a curve  $R_{2,2,2}$  of order  $\frac{3}{2}(n - 4)(n - 5)(3n^2 + 5n - 14)$ .

We consider now the system  $[c^n]$  of the curves possessing a tangent  $t_{2,2,2}$ , and determine the order of the locus of the points  $Q$ , which each  $c^n$  has moreover in common with its  $t_{2,2,2}$ . The system  $[c^n]$  has as index  $(n - 3)(n - 4)(n - 5)(n^2 + 3n - 2)$ ; for this is the number of  $c^n$  of the pencil determined by a point  $P$  possessing a  $t_{2,2,2}$ <sup>1)</sup>. The index of the system  $[t_{2,2,2}]$  is (§ 7)  $2n(n - 3)(n - 4)(n - 5)$ . To the figure produced by  $[c^n]$  and  $[t_{2,2,2}]$  the curve  $(R)_{2,2,2}$  belongs twice. For the order of  $(Q)$  we find consequently  $(n - 3)(n - 4)(n - 5)(n^2 + 3n - 2) + 2n^2(n - 3)(n - 4)(n - 5) - 3(n - 4)(n - 5)(3n^2 + 5n - 14)$  or  $(n - 4)(n - 5)(n - 6)(3n^2 + 3n - 8)$ .

11. On each  $t_{2,2,2}$  we associate each of the points of contact  $R$  to each of the intersections  $Q$ , and consider the correspondence  $(MR, MQ)$ . Its characteristic numbers are  $\frac{3}{2}(3n^2 + 5n - 14)(n - 4)(n - 5)(n - 6)$  and  $3(n - 4)(n - 5)(n - 6)(3n^2 + 3n - 8)$ . Each of the  $2n(n - 3)(n - 4)(n - 5)$  tangents  $t_{2,2,2}$  converging in  $M$ , represents apparently  $3(n - 6)$  coincidences. Taking this into consideration we find for the number of coincidences  $R \equiv Q$ , consequently for the number of tangents  $t_{2,2,3}$ ,  $\frac{3}{2}(n - 4)(n - 5)(n - 6)(5n^2 + 23n - 30)$ .

The correspondence between two points  $Q$  belonging to the same  $c^n$  determines in the pencil of rays  $(M)$  a symmetrical correspondence with characteristic number  $(3n^2 + 3n - 8)(n - 4)(n - 5)(n - 6)(n - 7)$ . To this each of the  $2n(n - 3)(n - 4)(n - 5)$  tangents converging in  $M$  belongs  $(n - 6)(n - 7)$ -times. Paying attention to this we find for the number of coincidences  $Q_1 \equiv Q_2$   $4(n - 4)(n - 5)(n - 6)(n - 7)(n - 1)(n + 4)$ . There are consequently  $(n - 4)(n - 5)(n - 6)(n - 7)(n - 1)(n + 4)$  quadruple tangents.

12. We shall now consider the system of the curves  $c^n$  possessing a tangent  $t_{2,3}$ , which touches it in a point  $R$ , and osculates it in a point  $I$ . In order to find the locus of the points  $S$ , which  $c^n$  has

<sup>1)</sup> T. p. 108.

moreover in common with  $t_{2,3}$ , we determine the order of the figure produced by the projective systems  $[c^n]$  and  $[t_{2,3}]$ . The former has as index  $3(n-3)(n-4)(n^2+6n-4)$  i.e. the number of  $c^n$  with a  $t_{2,3}$  appearing in a pencil<sup>1)</sup> of  $N$ . The index of  $[t_{2,3}]$  is (§ 3)  $9n(n-3)(n-4)$ . The figure produced contains the curve ( $R$ ) twice, the curve ( $I$ ) three times. For the order of  $S$  we find therefore

$$3(n-3)(n-4)(n^2+6n-4) + 9n^2(n-3)(n-4) - 6(n-4)(2n^2+5n-12) - 9(n-4)(n^2+6n-13) = 3(n-4)(n-5)(4n^2+7n-15).$$

By means of this result we can determine the number of twice osculating lines  $t_{3,3}$ . For this purpose we consider the correspondence ( $MR, MS$ ). Its characteristic numbers are

$$3(2n^2+5n-12)(n-4)(n-5) \text{ and } 3(4n^2+7n-15)(n-4)(n-5).$$

Each of the  $9n(n-3)(n-4)$   $t_{2,3}$  belonging to the pencil ( $M$ ) is  $(n-5)$ -fold coincidence, hence the number of coincidences  $R \equiv S$  is  $(n-4)(n-5)[(6n^2+15n-36) + (12n^2+21n-45) - 9n(n-3)] = (n-4)(n-5)(9n^2+63n-81)$ . But then the number of twice osculating tangents  $t_{3,3}$  amounts to  $\frac{9}{2}(n-4)(n-5)(n^2+7n-9)$ .

By means of the correspondence between the points  $I$  and  $S$  of the tangents  $t_{2,3}$  we can find back the number of tangents  $t_{2,4}$  found already in § 6. Analogously we obtain by means of the correspondence between two points  $S$  of the same  $t_{2,3}$  again the number of tangents  $t_{2,2,3}$  found in § 11.

**13.** If the net has a base-point  $B$ , the curves  $c^n$ , having an inflection in  $B$  are cut by their stationary tangents  $t$  in groups of  $(n-3)$  points  $T$ , lying on a curve  $(T)^{n+3}$  with sextuple point  $B$  (§ 5). This curve is of class  $(n+3)(n+2) - 30$ ; through  $B$  pass  $(n^2+5n-36)$  of its tangents. In the point of contact  $R$  of such a tangent the latter is touched by a  $c^n$ , which it osculates in  $B$ ; consequently  $B$  is a  $(n-4)(n+9)$ -fold point on the curve  $(I)_{2,3}$ .

The curves  $c^n$ , which touch in  $B$  at a ray  $d$ , form a pencil, consequently determine on  $d$  an involution of order  $(n-2)$ . As it possesses  $2(n-3)$  coincidences there are  $2(n-3)$   $c^n$ , which have  $d$  as bitangent, of which  $B$  is one of the points of contact. The second point of contact,  $R$ , coincides with  $B$  if  $d$  becomes fourpoint tangent, consequently  $B$  point of undulation. This occurs six times; hence the locus  $(R)_B$  of the points  $R$  is a curve of order  $2n$ , with sextuple point  $B$ .

Every straight line  $d$  cuts the  $c^n$ , which it touches in  $B$  and in  $R$ , moreover in  $(n-4)$  points  $S$ . In order to determine the locus

<sup>1)</sup> T. p. 106.

$(S)_B$  of these points, we associate each ray  $d$  to the  $2(n-3)$  curves  $c^n$ , to which it belongs, and consider the figure produced by the projective systems  $[c^n]$  and  $(d)$  thus determined.

Through a point  $P$  passes a pencil of  $c^n$ ; the base-point  $B$  is point of contact of  $(n-3)(n+4)$  bitangents; this number is the index of  $[c^n]$ . The order of the figure produced now amounts to  $(n-3)(n+4) + 2n(n-3) = (n-3)(3n+4)$ . To this the curve  $(R)_B$  apparently belongs twice; for the order of  $(S)_B$  we find therefore  $(n-3)(3n+4) - 4n$  or  $3(n+1)(n-4)$ .

As every  $d$ , outside  $B$ , contains  $2(n-3)(n-4)$  points  $S$ ,  $(S)_B$  will have in  $B$  a multiple point of order  $3(n+1)(n-4) - 2(n-3)(n-4)$  or  $(n+9)(n-4)$ .

**14.** Let us now consider the correspondence  $(MR, MS)$ , if  $R$  and  $S$  lie on the same ray  $d$  through  $B$ . To each ray  $MR$  belong  $2n(n-4)$  rays  $MS$ , each ray  $MS$  determines  $3(n+1)(n-4)$  rays  $MR$ . The ray  $MB$  contains  $2(n-3)$  points  $R$ , consequently represents  $2(n-3)(n-4)$  coincidences. The remaining ones, to the number of  $(n-4)(2n+3n+3-2n+6)$ , pass through points  $R \equiv S$ . So there are  $3(n-4)(n+3)$  rays  $d$ , which each touch a  $c^n$  in  $B$  and osculate it in a point  $I$ ; the curve  $(R)_{2,3}$  has consequently a  $3(n-4)(n+3)$ -fold point in  $B$ .

Now we pay attention to the symmetrical correspondence of the rays, which connect  $M$  with two points  $S$  belonging to the same  $c^n$ . The characteristic number is here  $3(n+1)(n-4)(n-5)$ , while  $MB$  represents  $2(n-3)(n-4)(n-5)$  coincidences. The remaining  $(n-4)(n-5)$   $[6(n+1) - 2(n-3)]$  lie in pairs on a *triple tangent*, which has one of its points of contact in  $B$ . From this we conclude that the curve  $(R)_{2,2,2}$  possesses in  $B$  a  $2(n+3)(n-4)(n-5)$ -fold point.

**15.** Let  $D$  be node of an  $c^n$ ,  $t$  one of the tangents in  $D$ ,  $S$  one of the intersections of  $t$  with  $c^n$ . In order to find the locus of  $S$ , we associate to each nodal  $c^n$  its two tangents  $t$  and determine the order of the figure produced by it. The tangents  $t$  envelop the curve of ZEUTHEN; they form consequently a system with index  $3(n-1)^2$ ; for a pencil contains  $3(n-1)^2$  nodal curves. By means of the correspondence of the series of points, which the two systems determine on a line, we now find again the order of the figure produced. Considering that the locus of  $D$  belongs six times to it, we obtain as order of the curve  $(S)$   $3n(n-1)(2n-3) + 6(n-1)^2 - 18(n-1) = 3(n-1)(2n^2 - n - 8)$ . For  $n = 3$  we find 42 for it; the 21 straight lines of the degenerate curves must indeed be counted twice.

We now consider the correspondence  $(MD, MS)$ . Its characteristic numbers are  $3(n-1) \cdot 2(n-3)$  and  $3(n-1)(2n^2-n-8)$ , while each of the tangents  $t$  converging in  $M$ , apparently produces  $(n-3)$  coincidences. The remaining ones arise from coincidences  $D \equiv S$ , consequently from nodal curves, for which  $D$  has an inflection on one of its branches. It now ensues from  $6(n-1)(n-3) + 3(n-1)(2n^2-n-8) - 3(n-1)(n-3)(2n-3) = 3(n-1)(10n-23)$ , that *the net contains  $3(n-1)(10n-23)$  curves with a flecnodal point.*

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#### E R R A T U M.

In the Proceedings of the meeting of November 28, 1914.

p. 870 line 15 from the bottom: Add: Supplement N<sup>o</sup>. 37 to the Communications from the Physical Laboratory at Leiden.  
Communicated by Prof. H. KAMERLINGH ONNES.

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**January 28, 1915.**

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CONTENTS.

- J. P. KUENEN: "On the measurement of the capillary pressure in a soap-bubble", p. 946.
- II. KAMERLINGH ONNES, C. DORSMAN, and G. HOLST: "Isothermals of di-atomic substances and their binary mixtures. XV. Vapour-pressures of oxygen and critical point of oxygen and nitrogen". p. 950.
- E. MATHIAS, II. KAMERLINGH ONNES, and C. A. CROMMELIN: "The rectilinear diameter of nitrogen", p. 953.
- C. A. CROMMELIN: "Isothermals of di-atomic substances\* and their binary mixtures. XVI. Vapour-pressures of nitrogen between the critical point and the boiling point". (Communicated by Prof. H. KAMERLINGH ONNES), p. 959.
- A. SMITS and S. C. BOKHORST: "On the vapour pressure lines of the system phosphorus." III. (Communicated by Prof. J. D. VAN DER WAALS), p. 962.
- A. SMITS and S. C. BOKHORST: "Further particulars concerning the system phosphorus." (Communicated by Prof. J. D. VAN DER WAALS), p. 973.
- J. BOEKE: "On the termination of the efferent nerves in plain muscle-cells, and its bearing on the sympathetic (accessory) innervation of the striated muscle-fibre", p. 982. (With one plate).
- J. BOEKE: "On the mode of attachment of the muscular fibre to its tendonfibres in the striated muscles of the vertebrates", p. 989.
- J. DROSTE: "On the field of a single centre in EINSTEIN's theory of gravitation". (Communicated by Prof. H. A. LORENTZ), p. 998.
- F. E. C. SCHEFFER: "On gas equilibria, and a test of Prof. J. D. VAN DER WAALS JR.'s formula". II. (Communicated by Prof. J. D. VAN DER WAALS), p. 1011.
- A. F. HOLLEMAN: "The replacement of substituents in benzene derivatives", p. 1027.
- P. VAN ROMBURGH and Miss. D. W. WENSINK: "On the interaction of ammonia and methylamine on 2,3,4-trinitrodimethylaniline", p. 1034.
- C. H. SLUIJER: "The influence of the hydration and of the deviations from the ideal gas-laws in aqueous solutions of salts on the solidifying and the boiling points". (Communicated by Prof. A. F. HOLLEMAN), p. 1036.
- W. DE SITTER: "On the figure of the planet Jupiter", p. 1047.
- ERNST COHEN and W. D. HELDERMAN: "The Allotropy of Cadmium." V, p. 1050.
- ERNST COHEN and W. D. HELDERMAN: "Note on our paper: 'The Allotropy of Lead'. I, p. 1055.
- JAN DE VRIES: "Characteristic numbers for a triply infinite system of algebraic plane curves", p. 1055.
- J. P. KUENEN: "The diffusion-coefficient of gases and the viscosity of gas-mixtures." p. 1068.
- Errata, p. 1073.

**Physics.** — “*On the measurement of the capillary pressure in a soap-bubble.*” By Prof. J. P. KUENEN. (Communication N<sup>o</sup>. 145a from the Physical Laboratory at Leiden).

(Communicated in the meeting of December 30, 1914).

In the measurement of the pressure in a soap-bubble by means of an open liquid gauge the peculiar case may present itself, that the measurement becomes impossible owing to the condition becoming unstable. This fact accidentally came under my notice, when an attempt was being made to increase the accuracy of the measurement of the comparatively small pressure by the use of a micro-manometer; in this instrument the construction of which is otherwise of no importance for the present purpose the pressure to be measured acts on a large liquid surface (about  $47 \text{ cm}^2$ ) which on a change of pressure is displaced over the same distance, as if the instrument were a simple open water-gauge with two tubes of the same width. When this manometer was used, it appeared impossible to work with soap-bubbles of less than about 1 cm. diameter, as smaller bubbles always contracted of their own accord, though no leakage could be discovered in the apparatus, whereas with a gauge with narrow tubes a similar difficulty had never presented itself.

A consideration of the equilibrium-relations had to lead to the explanation of the phenomenon and it soon appeared, that it was connected with the change of volume in the gauge which accompanies the displacement of the liquid surface on a change of pressure. Starting from a condition of equilibrium between the surface-tension  $\sigma$  and the excess of pressure  $p - p_0$  ( $p_0 =$  atmospheric pressure), in which therefore  $p - p_0 = \frac{4\sigma}{r}$  ( $r =$  radius of bubble), and applying to the bubble a virtual change, say a diminution of the radius, the capillary pressure will increase and this will cause the liquid-surface in the gauge to descend, which in its turn involves an increase of the volume. Now the condition will certainly be unstable, if this increase of volume exceeds the diminution of volume given to the soap-bubble; because in the enlarged volume the pressure of the gas will be smaller and this decrease will cause a further contraction of the soap-bubble. It now also becomes clear, why the phenomenon was observed for the first time in using the wide gauge: the increase of volume which goes with an increase of pressure is much more prominent in this case.

One might be inclined to draw the conclusion, that the limit

between stable and unstable must be found in that condition, where the two changes of volume referred to are equal to each other. This conclusion appears to be incorrect, however, when the condition for stability or non-stability is accurately established. The nature of the equilibrium depends upon, whether in a virtual contraction of the soap-bubble the pressure caused by the surface-tension increases less or more than the pressure of the gas, and the latter is given by BOYLE'S law, if the temperature is supposed to remain constant. In the former case the gas-pressure prevails, when the bubble contracts, and the condition is stable, in the latter case the condition is unstable.

Calling the volume of the space from the orifice of the tube, on which the bubble is blown, to the liquid surface, when the pressures inside and outside are equal,  $v_0$ , the displacement of the liquid  $h$  and the cross-section of the manometer-tube  $O$ , and treating the bubble as a complete sphere, the total volume is

$$v = v_0 + \frac{4}{3} \pi r^3 + hO,$$

whereas,  $d$  being the density of the liquid in the gauge,

$$2hdg = p - p_0 = \frac{4\sigma}{r},$$

so that

$$v = v_0 + \frac{4}{3} \pi r^3 + \frac{2\sigma O}{rdg}.$$

The change of the capillary pressure is given by the relation

$$-\frac{d(p-p_0)}{dr} = \frac{4\sigma}{r^2},$$

whereas for the gas-pressure  $pv = c$ , so that

$$-\frac{dp}{dr} = -\frac{dp}{dv} \frac{dv}{dr} = \frac{c}{v^2} \left( 4 \pi r^2 - \frac{2\sigma O}{r^2 dg} \right) = \frac{p}{v} \left( 4 \pi r^2 - \frac{2\sigma O}{r^2 dg} \right)$$

and the condition will be stable or unstable, according to whether:

$$\frac{4\sigma}{r^2} < \frac{p}{v} \left( 4 \pi r^2 - \frac{2\sigma O}{r^2 dg} \right).$$

The same result is obtained from the condition, that in stable, respectively unstable equilibrium the free energy  $\psi$  of a closed system at constant temperature is a minimum, respectively a maximum. In our case  $\psi$  may be written in the form:

$$\psi = 8 \pi r^2 \sigma - c \log v + O h^2 dg + p_0 v,$$

whence:

$$\frac{d\psi}{dr} = 16 \pi r \sigma - \frac{c}{v} \frac{dv}{dr} + 2O h dg \frac{dh}{dr} + p_0 \frac{dv}{dr},$$

or after reduction

$$\frac{d\psi}{dr} = 16 \pi r \sigma - (p - p_0) 4 \pi r^2.$$

The condition of equilibrium  $\frac{d\psi}{dr} = 0$  gives the relation  $p - p_0 = \frac{4\sigma}{r}$ , made use of above.

We have further:

$$\begin{aligned} \frac{d^2\psi}{dr^2} &= 16 \pi \sigma - (p - p_0) 8 \pi r - \frac{dp}{dv} \frac{dv}{dr} 4 \pi r^2 = \\ &= -16 \pi \sigma + \frac{p}{v} \left( 4 \pi r^2 - \frac{2\sigma O}{r^2 dg} \right) 4 \pi r^2 \gtrless 0, \end{aligned}$$

which leads to the same inequality as arrived at above.

This relation reveals the remarkable fact, that even without the manometer the condition may be unstable, viz. when

$$\frac{4\sigma}{r^2} > \frac{p}{v} 4 \pi r^2 \quad \text{or} \quad r^4 < \frac{\sigma v}{\pi p}.$$

The value of  $r$  is limited by the circumstance, that it cannot be smaller than the radius of the tube to which the soap-bubble is blown, and, as  $p$  is of the order  $10^6$ ,  $\sigma$  for a soap-solution being about 25, the unstable condition cannot be realized unless with a large volume  $v$ . In order to test the above result a carboy of 30 liters ( $v = 30000$ ) was attached to the apparatus without gauge: in this case the condition becomes  $r < 0.7$  cm. That the condition was unstable, was manifested in blowing the bulb in the fact, that, as soon as the bubble exceeded the half-sphere, it blew itself up quickly to a considerable size. In diminishing the bulb below the given limit by letting out air the unstable nature of the equilibrium showed itself less clearly. The bubble sometimes remained for a considerable time without appreciable change in size; this must be due to a retardation the nature of which was not fully explained: as a rule by tapping the tube the bubble could be made to contract in accordance with expectation.

As shown by the above complete relation, the addition of the gauge on which the second term on the right-hand side depends will make it possible to realize the unstable condition with a much smaller volume, the more easily, the larger the section  $O$  of the

manometer is. Calculation shows, that even with  $v = 1000$  cc. the left hand side of the relation is much too small to have an effect, and the condition thus becomes with near approximation

$$4\pi r^2 > \frac{2\sigma O}{r^2 dg} \quad \text{or} \quad r^4 > \frac{\sigma O}{2\pi dg}.$$

In this case the condition for the transition to the unstable condition agrees, as is at once seen, with that mentioned in the beginning, that the change of volume of the bubble becomes smaller than that of the gauge.

In order to make the phenomenon even more prominent than with the open gauge, the latter was replaced by a large funnel which was connected to the apparatus and placed upside down in a large trough of water with its rim just below the water level. The area  $O$  was now  $64\pi$  cm<sup>2</sup> and moreover the displacement  $h$  was almost completely confined to the water-surface inside the funnel (as the level in the large trough does not change appreciably) and thus twice as large as with the open gauge with tubes of the same width. In this case,  $hdg = p - p_0$  and the condition becomes

$$r^4 > \frac{\sigma O}{\pi dg},$$

which with the numerical values given above leads to  $r < 1.1$  cm. as the transition to the unstable condition. In agreement with this result the experiment showed, that the bubble could not be made smaller than 2 cm. in diameter without the bubble gradually beginning to contract.

The contraction continues, as long as the bubble is larger than a half-sphere; beyond this state  $r$  begins to increase; the capillary pressure thus begins to diminish and the contraction will cease, when the capillary pressure has become equal to the pressure exerted by the gas present. The condition can now but be stable, as a further contraction involves a diminution of the capillary pressure and therefore a diminution of the volume in the gauge and an increase of the gas-pressure.

By means of the above relations the further question may be solved whether an increase of  $c$  in the formula  $pv = c$ , i.e. an increase of temperature or of the quantity of gas, will make the bubble larger or smaller. The relation:

$$\frac{dc}{dr} = p \frac{dv}{dr} + v \frac{dp}{dr} = p \frac{dv}{dr} - v \frac{4\sigma}{r^2}$$

shows, that in the stable condition the bubble will increase and conversely in the unstable condition.

**Physics.** — “*Isothermals of di-atomic substances and their binary mixtures. XV. Vapour-pressures of oxygen and critical point of oxygen and nitrogen.*” By H. KAMERLINGH ONNES, C. DORSMAN, and G. HOLST. (Communication N<sup>o</sup>. 145*b* from the Physical Laboratory at Leiden). (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated in the meeting of December 30, 1914).

### 1. *Apparatus and method.*

The vapour-pressures of oxygen at twelve different temperatures and the critical points of oxygen and nitrogen were determined by means of the apparatus which was first used by KAMERLINGH ONNES and HYNDMAN for unpublished investigations of oxygen, of which those published on this occasion form a repetition, and later on by CROMMELIN for a determination of vapour-pressures of argon. A detailed description was given in Comm. Phys. Lab. N<sup>o</sup>. 115 (Meeting of April 1910). In the piezometer is an electromagnetic stirrer according to KUENEN.

In order to make a study of the critical phenomena possible two narrow slits of the vacuum-vessel of the cryostat were left unsilvered. (Compare Comm. N<sup>o</sup>. 83. Meetings of Dec. 1902 and Febr. 1903. As mentioned in an erratum to Plate IV § 6, the vessel  $B'$  is drawn 18 cms longer than it was). Besides the piezometer there were two  $Pt$ -resistance thermometers in the cryostat which had both been directly compared with the hydrogen-thermometer. One of them (the other one  $Pt_j$  broke afterwards) was  $Pt_i$  of Comm. N<sup>o</sup>. 141*a* § 6, the same which was also used in the measurements concerning the diameter. The pressures above 20 atm. were measured with the closed hydrogen-manometer described in Comm. N<sup>o</sup>. 97*a* § 3. At lower pressures the open gauge of KAMERLINGH ONNES (Comm. N<sup>o</sup>. 44) was used.

In order to determine the critical constants small portions of isothermals were studied in the neighbourhood of the critical point. At temperatures below the critical temperature starting from a suitably chosen volume and compressing by small amounts a condition can be found by sufficient compression in which the next compression produces condensation; at temperatures above the critical temperature condensation cannot occur.

The critical point having been approximately determined in this way, the observations were repeated within narrower limits of pressure, at temperatures ascending by about  $\frac{1}{20}^{\circ}$  C. Beginning with a pressure below the critical pressure and proceeding along an

isothermal still smaller portions than before were taken by applying very small compressions. This process was continued until the critical pressure had been passed. After each compression some minutes were allowed to elapse, the substance being meanwhile thoroughly stirred with the electromagnetic stirrer, so that all traces of the heat developed by the adiabatic compression must have disappeared by the time it was ascertained whether condensation had taken place. After this the process was repeated in the reverse direction, gradually going down to lower pressures and ascertaining, what at each subsequent stage the effect was of a very small expansion, say of  $\frac{1}{10}$  of an atmosphere. As before after each expansion some time was allowed to pass, until it could be assumed, that the gas had returned to the original temperature. If we proceed in this way along an isothermal immediately above  $T_k$  it is found that in the neighbourhood of the critical condition at a small sudden, and therefore approximately adiabatic, expansion a liquid surface appears which disappears again with thorough stirring. If the isothermal lies below  $T_k$ , the meniscus produced by a very small expansion does not disappear on stirring.

As the critical point we ultimately took the point at which on a small expansion the meniscus appeared half way up the tube and where conversely as the temperature re-established itself it disappeared again at the same level. By this procedure the critical temperature could easily be determined to about  $\frac{1}{20}^\circ$  C. On a future occasion this method will be published in greater detail with the addition of numerical results.

It is worth mentioning that we did not succeed in observing the critical opalescence <sup>1)</sup>, although in the experiments temperature and pressure were completely under control and the distinctness of observation of the phenomena in the piezometer-vessel left nothing to be desired as regards the permanent transparency of the walls. Our result, that the opalescence if existing must be very slight, derives its weight from the fact, that we looked for it with special attention, because on a former occasion one of us (H. K. O.) had been struck by its absence.

§ 2. *Preparation of the substances.* The oxygen was prepared from

<sup>1)</sup> These experiments were made in 1911. Looking through the literature of the subject, while writing this communication, we find the absence of the critical opalescence mentioned for the first time in a preliminary note by E. CARDOSO, *Eléments critiques et phases coëxistantes des gaz permanents* (II). Arch. d. Sc. phys. et nat. 15 Août 1914 p. 137.

CARDOSO adds a partial explanation based upon SMOLUCHOWSKI'S theory in connection with the law of corresponding states.

pure, recrystallized potassium permanganate, by heating in an apparatus which was completely of glass, and leading the gas over heated platinized asbestos. The apparatus which had served the same purpose in Comm. N<sup>o</sup>. 78 §11, had been improved by Dr. C. A. CROMMELIN when reconstructed, in that the tubes for drying and for absorbing the carbon dioxide had been replaced by an arrangement which allowed the gas to be condensed by cooling with liquid air and the liquid obtained to be re-evaporated (comp. Comm. N<sup>o</sup>. 117). A description of the apparatus will be given on a future occasion.

The nitrogen was prepared in the Pharmaceutical Laboratory under the supervision of Professor VAN ITALLIE, to whom we hereby express our hearty thanks. The method of preparation was by boiling a solution of sodiumnitrite and sodiumsulphate with ammonia; the nitrogen was then led over sulphuric acid in order to keep back ammonia that might be carried over.

The purity of both substances was checked by condensation experiments (comp. Comm. N<sup>o</sup>. 145*d*), when it appeared that the vapour-pressure between the beginning and the end of the condensation did not rise by more than a few hundredths of an atmosphere.

§ 3. *Results.* The results are contained in the following tables.

T A B L E I.

Vapour pressure of oxygen.		
$\theta = T - T_0^{\circ} \text{ C.}$	$T$ in KELVIN degrees	$p$ in atm.
$-154.91^{\circ} \text{ C.}$	$118.18^{\circ} \text{ K.}$	9.096
149.29	123.80	12.506
138.98	134.11	21.328
138.95	134.14	21.342
135.99	137.10	24.528
130.67	142.42	30.914
125.31	147.78	38.571
121.36	151.73	45.138
121.35	151.74	45.142
121.33	151.76	45.217
120.04	153.05	47.258
118.70	154.19	49.640

TABLE II.

Critical point of oxygen.		
$\theta_k = -118^{\circ}.84 \text{ C.}$	$T_k = 154^{\circ}.25 \text{ K.}$	$p_k = 49.713 \text{ atm.}$
Critical point of nitrogen.		
$\theta_k = -147^{\circ}.13 \text{ C.}$	$T_k = 125^{\circ}.96 \text{ K.}$	$p_k = 33.490 \text{ atm.}$

In the mean time we confine ourselves to communicating the numerical results and we will only add, that using the critical values obtained for oxygen the critical coefficient

$$K_{41} = \frac{RT_k}{p_k v_{kd}}$$

where  $v_{kd}$  is the critical volume derived from the diameter, is now found to be 3.419 instead of the previous value 3.346 deduced by MATHIAS and KAMERLINGH ONNES using incorrect data found elsewhere in the literature on the subject. (Comm. N<sup>o</sup>. 117).

The new value is no longer abnormally small when compared with that of normal substances of higher critical temperature and very nearly the same as that of argon 3.424 (Comm. N<sup>o</sup>. 131*a*).

**Physics.** — “*The rectilinear diameter of nitrogen*” By E. MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN. (Communication N<sup>o</sup>. 145*c* from the Physical Laboratory at Leiden.)

(Communicated in the meeting of December 30, 1914).

§ 1. *Introduction.* This communication is a continuation of the investigation undertaken in the Leiden Laboratory on the diameter for substances of low critical temperature and simple molecular structure, which was begun with oxygen<sup>1)</sup> and continued with argon<sup>2)</sup>. The object and the importance of these investigations were fully gone into in the paper on the diameter of oxygen and we need not recur to this here. For the further continuation of this research helium, hydrogen, and neon did not seem very suitable at present in view of the greater experimental difficulties, which

<sup>1)</sup> E. MATHIAS and H. KAMERLINGH ONNES, Proc. Febr. 1911, Comm. N<sup>o</sup>. 117.

<sup>2)</sup> E. MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN, Proc. Oct. and Dec. 1911 and Jan. 1912, Comm. N<sup>o</sup>. 131*a*.

have been partly, but not entirely surmounted. The obvious choice lay between nitrogen and carbon monoxide and it fell on nitrogen partly because for this substance more thermodynamical data are available than for carbon monoxide, whereby the importance of the investigation is much enhanced and partly because we could use the very pure nitrogen, with which determinations of the critical constants<sup>1)</sup> had been made. A separate experiment<sup>2)</sup> showed that the nitrogen was indeed of very high purity.

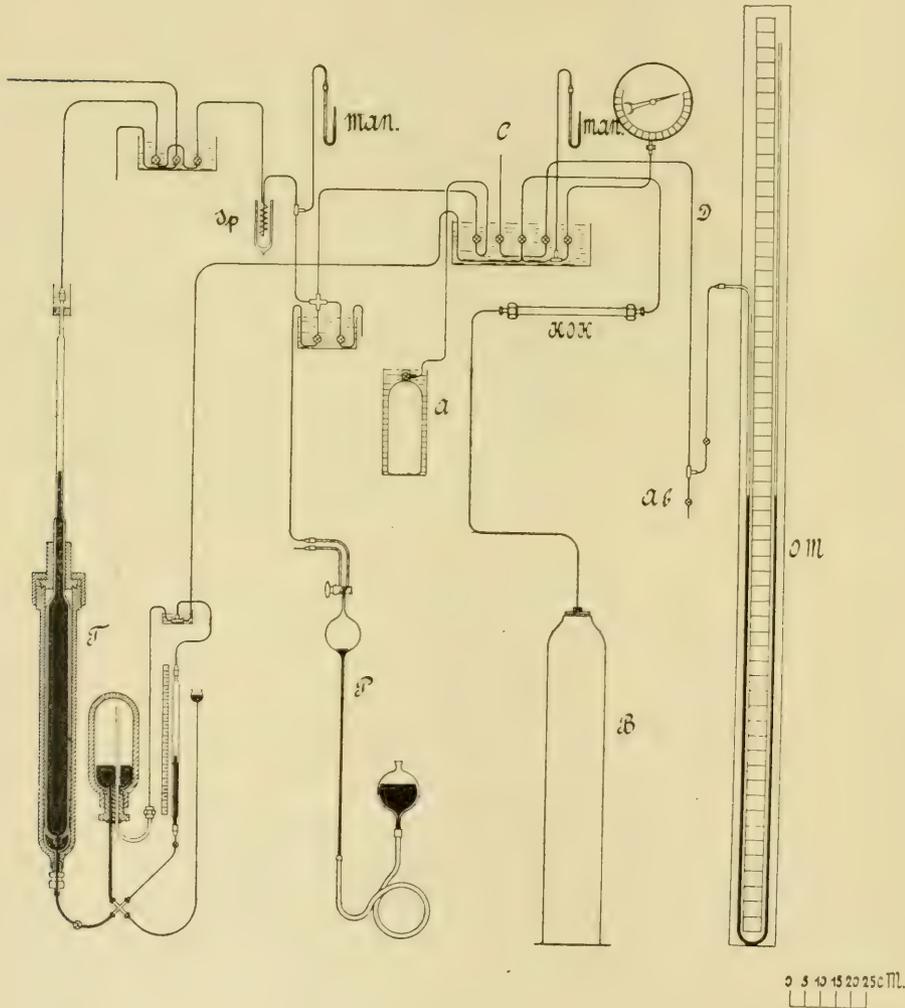


Fig. 1.

§ 2. *Apparatus.* The apparatus were practically the same as used for the determination of the diameter for argon; we, therefore,

<sup>1)</sup> This number of the Proc., H. KAMERLINGH ONNES, C. DORSMAN, and G. HOLST, Comm. N<sup>o</sup>. 145*b*.

<sup>2)</sup> Comp. this number of the Proc. C. A. CROMMELIN, Comm. N<sup>o</sup>. 145*d*.

refer to the communication quoted above. For the sake of completeness we will mention two small improvements<sup>1)</sup>:

1. The tube of the glass compression vessel  $a_1$  was made much longer in order to preclude all danger of the mercury when it rises quickly penetrating into the metal capillaries.

2. In the connection between the small high-pressure reservoir  $a$  and the compression vessel  $a_3$ , (by the taps  $c_{10}$ ,  $c_{13}$ ,  $k_9$ , and  $k_{20}$ ) a glass pipette of about one litre was introduced by means of a  $\pi$ -piece, so as to make it possible to transfer the nitrogen to the compression vessel in measured quantities.

These two improvements have added considerably to the certainty and convenience with which the apparatus could be manipulated.

§ 3. As regards the method of conducting the experiments we may also in the main refer to the previous paper.

The vapour-pressure measurements, which are needed for the calculation of the corrections, were not made during the diameter-determinations this time, but in a separate series of experiments, which will form the subject of a separate communication by one of us.<sup>2)</sup>

The temperature was again measured and at the same time kept constant by means of two platinum-thermometers  $Pt_{10}$  and  $Pt_{11}$ , which had been compared shortly before the measurements with the standard platinum-resistance-thermometer  $Pt_I$ . The latter had not long ago been once more very carefully compared with the hydrogen-thermometer<sup>3)</sup>, so that the temperature-measurement in our determinations must have satisfied very high requirements. The agreement of the two resistance-thermometers used left indeed nothing to be desired. In these measurements we were assisted by Mr. P. G. CATH, phil. nat. cand., whom we gladly hereby express our thanks for his coöperation.

4. *Calculations.* As regards these we may again refer to the previous communication. The reductions for the dead spaces at low temperature could not be made with the same certainty as in the case of argon; for the latter substance extensive series of observations of isotherms for low temperatures<sup>4)</sup> were available, whereas for nitrogen the same data are at present entirely lacking. We were

<sup>1)</sup> Comp. fig. 1 which is the improved form of the right-hand part of fig. 1 in Comm. N<sup>o</sup>. 131a.

<sup>2)</sup> C. A. CROMMELIN, This number of the Proc., Comm. N<sup>o</sup>. 145d.

<sup>3)</sup> KAMERLINGH ONNES and G. HOLST, Proc. Sept. 1914, Comm. N<sup>o</sup>. 141a.

<sup>4)</sup> H. KAMERLINGH ONNES and C. A. CROMMELIN, Proc. Dec. 1910, Comm. N<sup>o</sup>. 118b, and C. A. CROMMELIN, Dissertation, Leiden. 1910.

thus compelled to make use of the general reduced equation of state VII. 1. <sup>1)</sup> which in the region in question does not yet appreciably deviate from the special equation of state for argon VII.A. 3. <sup>2)</sup> which might otherwise have been preferable. This comes to the same as assuming, that nitrogen at the reduced temperatures under consideration corresponds to ether and isopentane.

For the calculation of the capillary corrections for the liquid nitrogen the observations by BALY and DONNAN <sup>3)</sup> were again utilized.

As the normal specific mass of nitrogen we have adopted the value 1.2514 grms. per Liter, as found in complete agreement by RAYLEIGH <sup>4)</sup> and by LEDUC <sup>5)</sup>.

Finally it should be mentioned, that the vapour-densities at the lowest 5 temperatures were not measured, but were calculated from the equation VII. 1.

5. *Results.* The results are represented graphically in fig. 2 and put together in the following table.

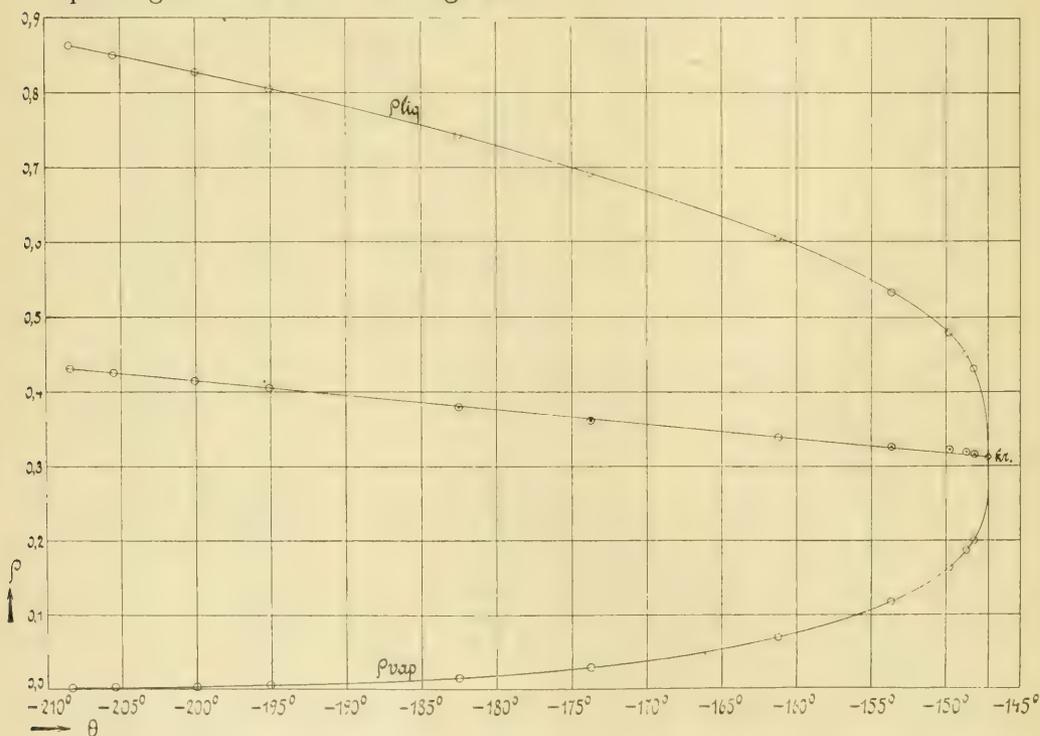


Fig. 2.

<sup>1)</sup> Comm. Leiden. Suppl. N<sup>o</sup>. 19, May 1908.

<sup>2)</sup> H. KAMERLINGH ONNES and C. A. CROMMELIN, Proc. June 1912, Comm. 128.

<sup>3)</sup> E. C. C. BALY and F. G. DONNAN, Journ. of the Chem. Soc. (Trans.) 81 (1902) p. 907.

<sup>4)</sup> Lord RAYLEIGH, Proc. R. S. 62 (1897) p. 204.

<sup>5)</sup> A. LEDUC, C. R. 126, (1898), p. 413.

Bath	$\theta$ Centigrade scale in Kel- vin degrees	$\rho_{\text{liq.}\Gamma}$	$\rho_{\text{vap.}\Gamma}$	$D_{\rho\Gamma}$ obs.	$D_{\rho\Gamma}$ calc.	obs.—calc.
O <sub>2</sub>	— 208.36	0.8622	0.00089	0.4316	0.4308	+ 0.0008
O <sub>2</sub>	— 205.45	0.8499	0.00136	0.4256	0.4251	+ 5
O <sub>2</sub>	— 200.03	0.8265	0.00278	0.4146	0.4145	+ 1
O <sub>2</sub>	— 195.09	0.8043	0.00490	0.4046	0.4048	— 2
O <sub>2</sub>	— 182.51	0.7433	0.01558	0.3794	0.3802	— 8
CH <sub>4</sub>	— 173.73	0.6922	0.02962	0.3609	0.3630	— 21
CH <sub>4</sub>	— 161.20	0.6071	0.06987	0.3385	0.3385	0
C <sub>2</sub> H <sub>4</sub>	— 153.65	0.5332	0.1177	0.3255	0.3237	+ 18
C <sub>2</sub> H <sub>4</sub>	— 149.75	0.4799	0.1638	0.3219	0.3161	+ 58
C <sub>2</sub> H <sub>4</sub>	— 148.61	0.4504	0.1862	0.3183	0.3138	+ 45
C <sub>2</sub> H <sub>4</sub>	— 148.08	0.4314	0.2000	0.3157	0.3128	+ 29

In the table  $\rho$  is the density and  $D$  the ordinate of the diameter; liq. and vap. refer to the liquid and the saturated vapour, and the index  $T$  indicates that the density is given in grammes per cc.).<sup>1)</sup>

The ordinates of the diameter are calculated from the formula:

$$D_{\rho\Gamma} = 0.022904 - 0.0019577 \theta.$$

The coefficients in this formula were calculated by the method of least squares from all the observations with the exception of those at  $-149^{\circ}.75$ ,  $-148^{\circ}.61$  and  $-148^{\circ}.08$ . The reason, why these three observations were not used in the calculation of the coefficients, will appear later on.

§ 6. *Discussion.* As appears from the table and even more plainly from figure 2 the deviations from the calculated rectilinear diameter<sup>2)</sup> are (1) systematic (2) near the critical point fairly considerable. It would be possible to distribute the deviations more evenly over the entire diameter by taking up the three observations which we have just referred to in the calculation of the coefficients; we have, however, preferred the method of calculation as given above, because

<sup>1)</sup> For the notations see also H. KAMERLINGH ONNES and W. H. KEESOM, Enc. math. W. ss. V. 10. Comm. Suppl. N<sup>o</sup>. 23.

<sup>2)</sup> In a preliminary note "Éléments critiques et phases coëxistantes des gaz permanents" (Arch. d. Sc. phys. et nat. Genève, 15 Aug. 1914, pg. 137) without numerical data E. CARDOSO mentions, that the diameters of oxygen and nitrogen are rectilinear up to the critical point.

in that manner the very approximately rectilinear character of a large part of the diameter shows better and also because by that method the critical density  $\rho_{kd}$  is obtained in the most rational way. Leaving out the deviations in the neighbourhood of the critical temperature and confining ourselves to those which refer to the direction of the diameter from (3) below the critical temperature downwards, it may be remarked, that these deviations although somewhat larger than those found with many other substances still in their general character do not differ from those shown by say carbon-dioxide and argon; the latter substances also possess at the lower temperatures a diameter which is convex on the side of the temperature-axis.

As regards the deviations near the critical point, although apparently they increase systematically, we cannot help being surprised at the exceptionally high amount of them (nearly 2%). A systematic fault of the apparatus or the method of working, although in the region of the higher temperatures our apparatus does not guarantee the same degree of accuracy which we may consider as assured in the region of the lower temperatures, may be considered as excluded by the results obtained with oxygen and argon. Again although the manner in which in the absence of all experimental material concerning the isotherms of nitrogen at low temperatures we were obliged to apply the corrections for the dead spaces in the glass capillary in the cryostat (and therefore at the low temperature) is open to some objection<sup>1)</sup>, still deviations of the said magnitude cannot thereby be explained.

In fact these corrections need not be known with more than a very small relative accuracy. It would be less improbable to look for the explanation in the presence of some admixture whose influence was too small to make itself felt in the test referred to by means of evaporation under constant pressure. Taking everything into account we consider it probable, that the large deviations do not find their explanation in the uncertainties of observation or calculation, but are connected with the deviation of the critical point from the extrapolated vapour-pressure curve. In order to find a conclusive answer to the questions raised here, a special investigation will be needed of the diameter of nitrogen in the immediate neighbourhood of the critical point with apparatus specially constructed for the purpose, as also in general a thermodynamical investigation in that region in which amongst other things the mixing of the phases by stirring will have to be provided for.

<sup>1)</sup> Comp. above § 4.

The coefficient of inclination of the diameter is:

$$b_{dT} = -0.0019577,$$

and thus a good deal smaller than the coefficients of argon ( $-0.0026235$ ) and of oxygen ( $-0.002265$ ).

The "undisturbed" *critical density* derived from the diameter using as the critical temperature  $-147^{\circ}.13^1$ ) is found to be:

$$\rho_{kd} = 0.31096.$$

A comparison with the value for the "undisturbed" critical density which might be derived by the aid of the equation  $\left(\frac{\partial \rho}{\partial T}\right)_{r.c.} = \left(\frac{d\rho}{dT}\right)_{\text{coex. c.}}$  from the vapour-pressure curve and the isotherms near the critical point (as this was carried out for argon) is impossible for nitrogen, as isotherms are not available in the mean time.

The *critical coefficient* is

$$K_{4d} = 3.421,$$

a comparatively small value, as was to be expected in connection with the simple molecular structure of nitrogen, its deviation from the theoretical value  $\frac{8}{3}$  is in the same direction and to much the same degree as that of argon (3.424) and that of oxygen (3.419)<sup>2</sup>).

The liquid densities at the lower temperatures are in fairly good agreement with those found by BALY and DONNAN<sup>3</sup>), the differences being of the order of 1%.

**Physics.** — *Isothermals of di-atomic substances and their binary mixtures.* XVI. *Vapour-pressures of nitrogen between the critical point and the boiling point.* By Dr. C. A. CROMMELIN. (Communication N<sup>o</sup>. 145d from the Physical Laboratory at Leiden). (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of December 30, 1914).

The determination of the density-curves and the diameter of nitrogen<sup>4</sup>) offered a welcome opportunity for determining the vapour-pressures of nitrogen between the critical point and the boiling point, therefore in the region of the higher pressures, and thus making a contribution towards the knowledge of the equation of

<sup>1</sup>) H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST, This number of the Proc. Comm. 145b.

<sup>2</sup>) Calculated with the critical constants of Comm. 145b.

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

<sup>4</sup>) E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN, This number of the Proc., Comm. N<sup>o</sup>. 145c.

state of nitrogen at low temperatures. Moreover several of these data were required for the computation of the corrections of the diameter-measurements.

In the region here dealt with so far all experimental data were lacking, at least if we leave out of account two old determinations by v. WROBLEWSKI<sup>1)</sup>, which differ considerably from mine. Vapour-pressures have been measured by BALY<sup>2)</sup> between  $-196^{\circ}$  and  $-182^{\circ}$ , by FISCHER and ALT<sup>3)</sup> between  $-195^{\circ}$  and  $-210^{\circ}$  and by VON SIEMENS<sup>4)</sup> between  $-192^{\circ}$  and  $-205^{\circ}$ , but, as will be seen, they all refer to regions of low temperatures and pressures.

The nitrogen was liquefied in the same dilatometer and by the same compression-cylinder, which had been used in the diameter-measurements of argon and nitrogen. It should be mentioned, that this dilatometer was not provided with a stirring-arrangement, so that the determinations were made without stirring. It is possibly due to this circumstance, that the vapour-pressures of nitrogen seem to be a trifle less accurate than those of oxygen.<sup>5)</sup>

As in the previous measurements the temperature was determined by means of two platinum-thermometers which had been compared with the standard resistance-thermometer *Pt<sub>1</sub>*. As regards all this we may therefore refer to previous communications<sup>6)</sup>. The pressures above 20 atm. were determined by means of the closed hydrogen-manometer<sup>7)</sup>, those below 20 atm. with the open standard-manometer<sup>8)</sup>.

The calculations do not call for special remarks. The atmosphere at Leiden was taken equivalent to 75.9488 cms. mercury.

The nitrogen with which the experiments were made was, as mentioned in connection with the diameter-measurements, the same as was used for the determinations of the critical constants. By these determinations the purity of the substance had been submitted to a

1) S. v. WROBLEWSKI, C. R. 102. (1886) p. 1010.

2) E. C. C. BALY, Phil. Mag. (5) 49 (1900) p. 517.

3) K. T. FISCHER and H. ALT, Ann. d. Phys. (4) 9 (1902) p. 1149.

4) H. VON SIEMENS, Ann. d. Phys. 42. (1913) p. 871.

5) H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST, This number of the Proc. Comm. No. 145b.

6) E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN, Proc. Oct. and Dec. 1912 and Jan. 1913. Comm. No. 131a (argon) and these Proc. above Comm. No. 145c (nitrogen).

7) H. KAMERLINGH ONNES and H. H. F. HYNDMAN, Proc. April 1902. Comm. No. 78 (§ 17) and H. KAMERLINGH ONNES and C. BRAAK, Proc. March 1907, Comm. No. 97a (§ 3).

8) H. KAMERLINGH ONNES, Proc. Nov. 1898, Comm. No. 44.

severe test. The nitrogen was moreover once more tested for its purity in the apparatus itself. For this purpose the vapour-pressure was measured at a temperature which was kept constant (about  $-153^{\circ}$ ), first when only a drop of liquid was present in the appendix of the dilatometer and immediately afterwards with the dilatometer completely filled with liquid. The vapour-pressure was found in the two cases to be

25.38 and 25.41 atm.

This difference of about one thousandth of the total value is not far removed from the limits of accuracy of the observations and proves (1) that the nitrogen was very pure and (2) that the temperature-difference near the top and near the bottom in the cryostat must have been inappreciable.

In the further observations the liquid-surface was always brought to about the middle of the dilatometerbulb.

Date 1914	Number	$\theta$ (centigrade in KELVIN degrees).	$p_{\text{Obs.}}$ atm. int.	$p_{\text{calc.}}$	Obs.-calc. (abs.)	Obs.-calc. (%)
21 Febr.	X	— 148.85	30.364	30.631	— 0.267	— 0.9
"	IX	— 152.11	25.889	26.087	— 0.198	— 0.8
"	VIII	— 155.47	21.820	21.945	— 0.125	— 0.6
20 Febr.	VII	— 161.31	15.949	15.949	0.000	0.0
17 Febr.	V	— 173.58	7.3705	7.3705	0.0000	0.0
"	IV	— 179.18	4.8278	4.8632	— 0.0354	— 0.7
16 Febr.	I	— 182.47	3.7248	3.7117	+ 0.0131	+ 0.4
"	II	— 186.88	2.5067	2.4863	+ 0.0204	+ 0.8
"	III	— 191.88	1.4727	1.4727	0.0000	0.0

In the above table are given the results of the measurements and a comparison with a formula of the form

$$\log p = a + \frac{b}{T} + \frac{c}{T^2} + \frac{d}{T^3}$$

where  $T$  represents the absolute temperature, the coefficients having the values

$$\begin{aligned} a &= + 5.76381 \\ b &= - 853.522 \\ c &= + 54372.3 \\ d &= - 1783500 \end{aligned}$$

which satisfy the following values of the critical constants

$$p_k = 33.49 \text{ atm. and } T_k = 125.96 \text{ K}^1)$$

$$(\theta_k = T_k - T_0^\circ \text{ C} = -147.13 \text{ C. in Kelvin-degrees})$$

The circumstance, that the observations do not agree very well with the formula, finds its explanation, at least partly, in the fact, that the critical point falls a little outside the extrapolated vapour-pressure curve. The same fact occurs with the vapour-pressure curves of argon (CROMMELIN <sup>2</sup>), ether (RAMSAY and YOUNG <sup>3</sup>), isopentane (YOUNG <sup>4</sup>) normal octane (YOUNG <sup>5</sup>), carbon disulphide (BATTELLI <sup>6</sup>) in contrast with what is found with the great majority of vapour-pressure curves of other substances, with regard to the critical point.

A systematic inquiry into the cause of these deviations would be very desirable.

In conclusion I wish to thank Prof. H. KAMERLINGH ONNES most heartily for the continued interest shown in my work.

**Chemistry.** — “*On the vapour pressure lines of the system phosphorus.*” III. By Prof. A. SMITS and S. C. BOKHORST. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of December 30, 1914).

I. *Determinations of the vapour pressure of the violet phosphorus.*

In the preliminary investigation about the vapour tension of the violet phosphorus we found a vapour pressure line with a discontinuity at about 450°, which result seemed to confirm the existence of a transition point found by JOLIBOIS <sup>7</sup>) at  $\pm 460$ .

To get further certainty about the existence or non-existence of this transition point, it had to be examined whether really two branches intersecting each other, could be realized here. For this purpose it would be necessary to determine also a part of the metastable prolongations on either side of the transition point, and keeping this end in view we undertook the definitive investigation.

The preliminary experiments were made with a preparation N<sup>o</sup>. 1, which was obtained by heating pure white phosphorus with 0.1 % Iodine at  $\pm 300^\circ$  for 24 hours. This preparation was hard and

<sup>1</sup>) Comm. 145*b*.

<sup>2</sup>) C. A. CROMMELIN, Proc. May 1910 and Oct. 1913, Comm. 115 and 138*c* and Dissertation Leiden 1910.

<sup>3</sup>) W. RAMSAY and S. YOUNG, Phil. Trans A 178, (1887) p. 57.

<sup>4</sup>) S. YOUNG, Proc. phys. Soc. 1894/1895 p. 602.

<sup>5</sup>) S. YOUNG, Journ. Chem. Soc. 77 (1900) p. 1145.

<sup>6</sup>) A. BATTELLI, Mem. d. Ac. di Torino, (2) 41 I (1890) and 42 I (1891).

<sup>7</sup>) C. r 149, 287 (1909); 151, 382 (1910).

brittle, possessed a violet colour, and did not emit light in the dark.

We started again from the same preparation; it was heated in a tube of not readily fusible glass in vacuo for twelve hours at  $510^{\circ}$ , so above the supposed transition point, and then it was suddenly cooled. Then half of the tube was heated in a bath at  $200^{\circ}$ , to condense the white phosphorus that had deposited from the vapour in the colder upper end of the tube. After careful cooling the tube was cut in the middle, and the glass spring (pressure indicator) was filled with the red phosphorus obtained in this way. Then the glass spring was evacuated by means of the pump and heated in an asbestos jacket at  $\pm 150$  for an hour to be sure that all the air was expelled, and then fused to at the bottom. The heating should not be carried up higher than  $150^{\circ}$ , because else, as appeared later, a great disturbance of the internal equilibrium takes place in consequence of the pumping off of the most volatile molecule kind from the phosphorus, which disturbance is only gradually prevented at higher temperature.

That in this way we really succeeded in removing all the air from the glass spring appears from this that at the end of the determinations no appreciable zero point change of the glass spring could be demonstrated.

The vapour tensions determined with this phosphorus were much too high, higher than before, and presented a close resemblance with that of the white phosphorus for the lower temperatures. It followed from this that the white phosphorus had not been sufficiently removed from the preparation, and that a subsequent treatment had to follow to remove it completely.

In future the violet phosphorus was therefore extracted in a Soxhlet-apparatus with  $\text{CS}_2$  for 6 hours, and then treated with ammonia to remove the possibly formed phosphoric acid. Then the preparation was washed with absolute ether, and dried in a vacuum exsiccator<sup>1)</sup> over  $\text{P}_2\text{O}_5$ .

Now *three* preparations were made, which were all subjected to the same after-treatment, which we shall designate by:

*Preparation N<sup>o</sup>. 2* made from preparation N<sup>o</sup>. 1 by heating it once more with 0.1 % Iodine at  $375^{\circ}$  for six days, and then subjecting it to the said after-treatment.

*Preparation No. 3* prepared from white phosphorus by first heating it *without* Iodine at  $300^{\circ}$  for some hours, and then once more

<sup>1)</sup> In this after-treatment part of the pseudo-component soluble in the  $\text{CS}_2$  will of course be ejected from the mass, which is in internal equilibrium. This, however, is of no importance, as this is restricted to the surface-layer only.

heating the formed red phosphorus, after addition of 0.1 % I at 400° for 3 days, after which the said after-treatment was of course applied again.

*Preparation No. 4* prepared from white phosphorus by heating it at 550°, for 5 hours, without the addition of Iodine, followed by the known after-treatment.

These preparations, of which we thought ourselves justified in expecting that they had assumed internal equilibrium resp. at 375°, 400°, 550° gave the following vapour pressures.

TABLE I.

Preparation No. 2 Temp. of preparat. 375° Manometer No. 69		Preparation No. 3 Temp. of preparat. 410° Manometer No. 72		Preparation No. 4 Temp. of preparat. 550° Manometer No. 74	
Temp.	Pressure	Temp.	Pressure	Temp.	Pressure
290°	0.05 atm.	308.5°	0.08 atm.	308.5°	0.07 atm.
308.5	0.09 "	346	0.17 "	346	0.13 "
328	0.15 "	375.5	0.40 "	379.5	0.35 "
346	0.25 "	394.5	0.65 "	408.5	0.79 "
365	0.39 "	418	1.12 "	433.5	1.49 "
384.5	0.60 "	448.5	2.23 "	450.5	2.30 "
410	1.02 "	457.5	2.89 "	463.5	3.18 "
429	1.54 "	461.5	3.17 "	472.5	3.88 "
444.5	2.16 "	474.5	4.19 "	486.5	5.46 "
456	2.82 "				

In these determinations we took care that when it seemed that at constant temperature also the pressure had become constant, the vapour pressure was observed at the same temperature for 10 or 20 minutes more, to examine if it really did not change any more.

When considering the result found here, which is represented graphically in Fig. 1, we observe that the mentioned preparations do *not* give the same vapour pressure line, but that the curve lies lower as the preparation is prepared at higher temperature. This imperfect coincidence of the three vapour pressure lines suggests that the establishment of the internal equilibrium in the range of temperature passed through here, proceeds so slowly, that no internal

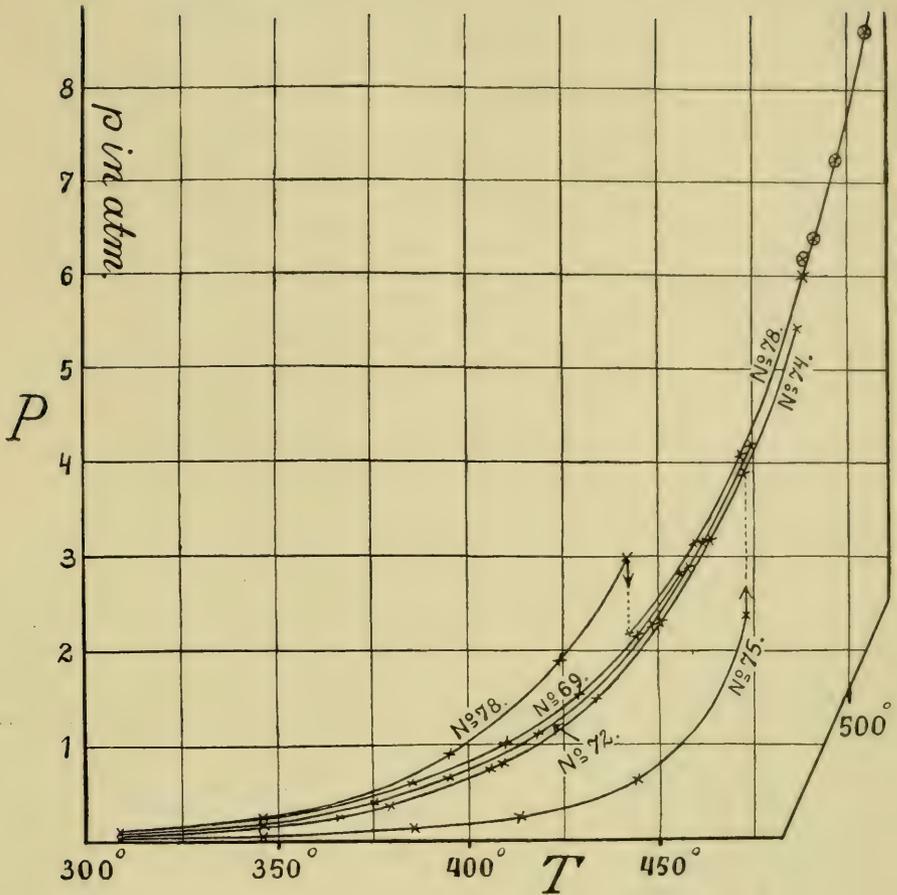


Fig. 1.

equilibrium can set in during the determination of the vapour pressure. That the preparation that has been prepared at the highest temperature, showed the lowest vapour tension, was further an indication that the establishment of the internal equilibrium was completest at the highest temperature of preparation. On closer examination of the observed vapour tensions it appeared later (see the following "communication") that this view was really the correct one.

It was now the question in how far the now found vapour pressure line was in harmony with the determinations of the vapour pressure of higher temperature.

For the vapour pressure at temperatures of  $505^\circ$  up to the triple point temperature the following values were found: (see page 966).

If we now represent this result together with that of Table I, preparation 4 in the same Figure, we get the following  $PT$ -diagram Fig. 2, from which it appears that the different determinations yield

TABLE II.

Preparation 1.		Glass spring
Temperature	Vapour tension	
505°	8.67 atm.	No. 11
515	10.43 "	" 1
522.5	11.61 "	" 7
578	34.35 "	" 7
581	36.49 "	" 12
587.5	41.77 "	" 12
588	42.10 "	" 7
589	42.6 "	" 30
Triple point 589.5	43.1 "	Pressure found by interpolation

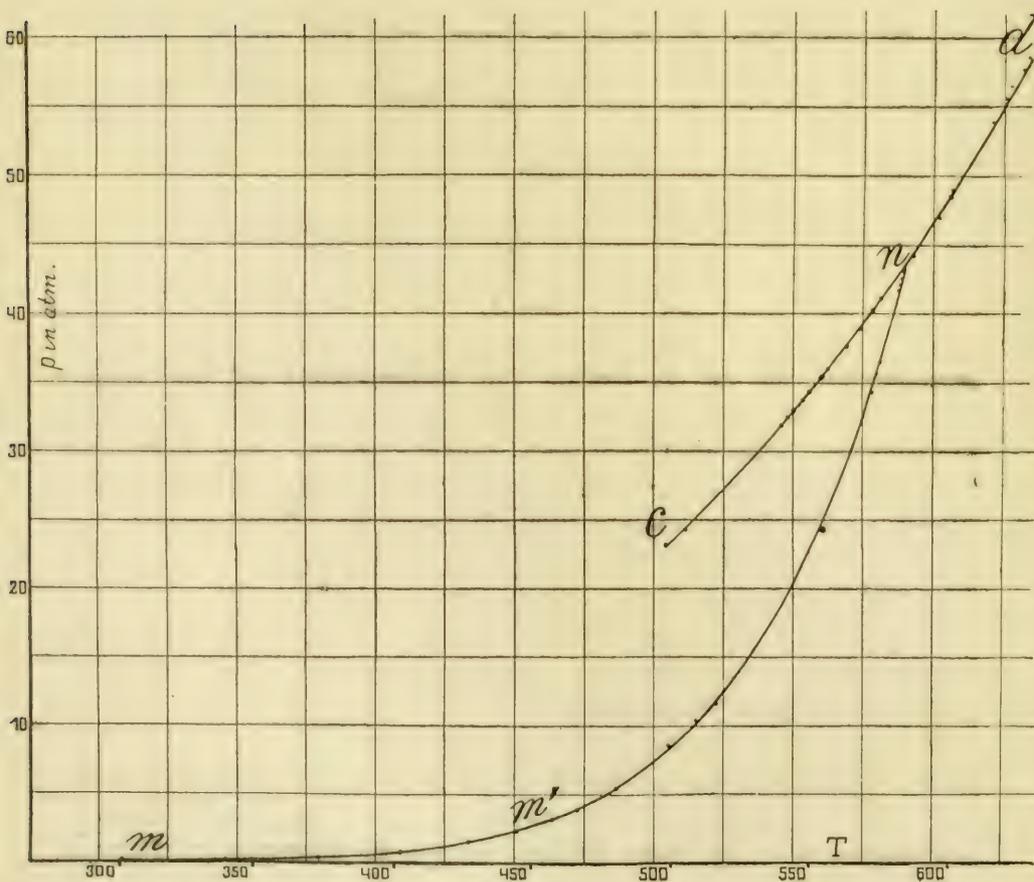


Fig. 2.

a curve with a perfectly regular course, so that there is no question of the occurrence of the discontinuity found before at  $450^{\circ}$ , which rendered the existence of a transition point, stating it mildly, very doubtful.

First of all it had to be examined what was the cause of the discrepant result of the earlier, preliminary determinations, and whether a preparation prepared in the same way again yielded such a line with a break at  $\pm 450^{\circ}$ .

To decide this question a new preparation N<sup>o</sup>. 5 was made, chiefly prepared in the same way as N<sup>o</sup>. 1; white phosphorus with 0,2% I was heated at  $400^{\circ}$  for 6 hours, then cooled very slowly to give the white phosphorus depositing from the vapour every possible opportunity to be converted to violet phosphorus.

This cooling lasted 14 hours, and when the tube was opened in the dark no emission of light could be observed. The obtained phosphorus was *not* extracted with  $\text{CS}_2$ , but only treated with water to remove oxidation products which might possibly be present, then washed with ether, and dried in a vacuum exsiccator over  $\text{P}_2\text{O}_5$ .

The vapour pressure line determined with this preparation in glass spring N<sup>o</sup>. 78, is represented in Fig. 1. We see from it that first four points were found which were much too high. In the determination of the fifth point a remarkable phenomenon was observed, which threw light on the vapour pressure line determined earlier. After the pressure had risen to 2,99 atm. at  $442^{\circ}$ , and had remained constant for five minutes, the pressure began to descend at first slowly, then more rapidly, and at last again more slowly.

When the phosphorus had been kept at the same temperature of  $442^{\circ}$  for two hours, the pressure had fallen to 2,21 atm., a value which agrees pretty well with that obtained with the preparations N<sup>o</sup>. 2, N<sup>o</sup>. 3, and N<sup>o</sup>. 4.

On continued investigation towards higher temperatures this agreement continued to exist, which follows from the subjoined table. (p. 968).

The result of this experiment is of great importance, for in the first place it follows from this that violet phosphorus prepared in the same way as for preparation N<sup>o</sup>. 5, so by the heating of white phosphorus with a trace of iodine, consists without after treatment of violet phosphorus, which was very nearly in internal equilibrium at the temperature of preparation, and that by the side of it a little white phosphorus is found, which has deposited on cooling from the vapour phase after the preparation of the violet phosphorus. It must now be attributed to the presence of this quantity of white phosphorus that in our preliminary investigation, just as in this last-mentioned

experiment, too high vapour tensions were found at the lower temperatures, and a discontinuity occurred in the neighbourhood of  $450^{\circ}$ .

Temp.	Vapour pressure in atmospheres
309°	0.12
346	0.23
395	0.90
424	1.90
442	2.21 (at first 2.99, then falling to 2.21)
459.5	3.15
471.5	4.10
488	6.00
424	1.55

} too high

Above  $360^{\circ}$  the white phosphorus is already converted with great velocity, but the concentration of the violet phosphorus in internal equilibrium differs so greatly from that of the liquid white and the gaseous phosphorus that a great internal chemical transformation of the volatile pseudo-component  $\alpha$  into the little volatile  $\beta$  must take place before the violet modification is formed. As long as this is not the case, the product of conversion will contain too much of the violet pseudo-component  $\alpha$ , hence the vapour tension will be too high.

Below  $450^{\circ}$  the *complete* transformation in the stable state of internal equilibrium of the solid substance (the violet phosphorus) requires much more time than we at first supposed, so that the vapour tension of a preparation which contained a little white phosphorus at first, was found too high below that temperature. It is true that we never proceeded to a following determination before the pressure had practically not changed for 15 minutes, but this time appeared to have been much too short. At higher temperature, however, this lapse of time was long enough to enable us to find out that the mass had not yet assumed internal equilibrium, for as was already mentioned above, the pressure began to descend already appreciably at  $442^{\circ}$ , and not until two hours later had it practically become constant, at which the pressure had reached a value which is in good harmony with the continuous vapour pressure line, which

was found with the preparations from which the white phosphorus had beforehand been quite removed by extraction with  $\text{CS}_2$ .

This result gave the solution of the difficulty, for it was now clear that the discontinuity found before at  $\pm 450^\circ$  was to be ascribed to this that only in the neighbourhood of this temperature the internal equilibrium begins to set in with such velocity that the internal transformation betrays itself by the setting in of a decrease of pressure within a few minutes.

At about the same temperature JOLIBOIS found a discontinuity in the curve of heating, and it is now perfectly certain that this irregularity must be accounted for in the same way as that found by us at first.

At  $500^\circ$  the velocity of the establishment of the internal equilibrium has become sufficiently great to render a reliable determination of the vapour tension of the violet phosphorus possible within one hour; and this is therefore the reason that the vapour tension with different preparations at temperatures above  $490^\circ$  are in good harmony with those of the preliminary investigation. Thus the vapour tension was once more determined with the same preparation N<sup>o</sup>. 5 at the temperature  $561^\circ$ , in which a pressure of 24,3 atm. was found.<sup>1)</sup>

As for the triple point pressure, it was determined in the following way. One of the pure preparations of violet phosphorus was heated very slowly in a perfectly evacuated tube of sparingly fusible glass placed in a glass beaker with molten potassium-sodium nitrate, the temperature being at the same time observed by means of a resistance thermometer and a thermo-element. Thus on repetition  $589.5$  was found for the *triple point temperature*. As now the molten violet phosphorus yields a straight line for  $T \ln P$  as function of  $T$ , it could be read with great accuracy from this line to what value of  $T \ln P$  the temperature of  $589.5^\circ$  corresponded; in this way the value 3246.6 was found for  $T \ln P$  at  $589.5^\circ$ , from which the value of the *triple point pressure* = 43.1 followed immediately, a value which is probably accurate within 0.5 atm.

With regard to the accuracy of the vapour pressure line we will here emphatically point out that the vapour tensions at temperatures below  $500^\circ$  will not agree perfectly with states of internal equilibrium, as at those temperatures the establishment of the internal equilibrium still proceeds too slowly. In consequence of this the equilibrium solid  $\rightleftharpoons$  vapour could, below  $400^\circ$ , only be approximated coming

<sup>1)</sup> This point has also been given in Fig. 2.

from lower temperatures, because passing from higher to lower temperature, the establishment of the equilibrium required far too much time. Owing to this we are unfortunately uncertain about the degree of the accuracy, but the error cannot be very great, as the preparations of different temperatures of preparation yield vapour pressure lines which, below  $500^{\circ}$ , differ comparatively little from each other in situation, with the exception of the very lowest points.

## 2. *Corroborations of the theory of allotropy.*

The theory of allotropy says that every phase of an allotropic substance exhibits the phenomenon of molecular allotropy, hence the violet phosphorus had also to be a state of internal equilibrium, which equilibrium is in general dependent on temperature and pressure.

To test this view the following experiment was made. By *sublimation in vacuo* it was tried to expel the more volatile pseudo component at a temperature at which the internal equilibrium sets in only very slowly, and the formation of the more volatile from the less volatile pseudo component takes, therefore, place with very slight velocity. If this succeeded, a substance would be obtained with a considerably smaller vapour tension than the preparation from which we had started.

Keeping this purpose in view part of the preparation N<sup>o</sup>. 4, with which the vapour pressure line with manometer N<sup>o</sup>. 74 had been determined was heated in a glass tube for two hours in the high vacuum of the Gaede-pump at somewhat more than  $360^{\circ}$ , during which small drops of liquid white phosphorus condensed against the colder part of the tube. After the tube had been cut in the middle, so that the violet phosphorus was separated from the white, a new glass spring N<sup>o</sup>. 75 was filled with the thus obtained violet P N<sup>o</sup>. 4a without any further treatment, and then we proceeded to the determination of the vapour tension.

It now really appeared that the vapour tension of this preparation was much too low, which is clearly indicated by the vapour pressure line N<sup>o</sup>. 75 in our PT-figure.

As this figure shows, this vapour tension line is not continued beyond  $473^{\circ}$ , because at this temperature a reading of the pressure was no longer possible on account of the continual slow rise of the vapour tension. Also this result was in perfect agreement with our expectations, because the internal equilibrium sets in already noticeably at  $473^{\circ}$ .

Now we might have continued the determination of the vapour

pressure at  $473^{\circ}$ , till the vapour pressure line which had been found before with preparation N<sup>o</sup>. 4, had been reached, but then the experiment would certainly have been continued for several hours, which gave rise to difficulties. To reach our purpose more quickly, the experiment was finished, and part of the same preparation N<sup>o</sup>. 4a, with which now a too low vapour pressure had been found, was heated with 0,15% Iodium at  $410^{\circ}$  for five hours, and then again subjected to the known after-treatment with CS<sub>2</sub>. Finally the vapour tension of this preparation N<sup>o</sup>. 4b was once more determined with the glass spring N<sup>o</sup>. 77 and then a vapour tension line was found which up to  $450^{\circ}$  perfectly coincided with the curve N<sup>o</sup>. 74, which had been found with the same material before the internal equilibrium had been disturbed. <sup>1)</sup>

*This experiment has, therefore, shown in the most convincing way that for violet phosphorus we have to do here with an internal equilibrium between at least two pseudo components, which greatly differ in volatility.*

### 3. *Designation of the unary stable solid state of the phosphorus, and the nature of red phosphorus.*

Our investigation has taught us that there is only one stable solid modification, and it is now the question by what name this modification will be denoted. In not very finely crystallized condition the colour of this stable solid state of the phosphorus is *violet*. If this substance is rubbed fine, however, the colour becomes dark red, and the greater the fineness, the lighter the colour. In the same way of preparing preparations of different colour are often obtained, which, however, had entirely to be ascribed to a difference in fineness, for it always appeared that though the colour was different, the preparations had the same vapour tension.

In virtue of this the name of *violet* phosphorus naturally suggests

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<sup>1)</sup> It should be noticed that when iodium is added to the *solid* red phosphorus, only a superficial internal equilibrium is obtained. If the vapour tension of the obtained solid substance is determined, the case can therefore occur that the vapour tension begins to deviate from the accurate curve at a definite temperature, in consequence of this that the quantity of the most volatile pseudo-component present has become insufficient, and the velocity of the internal conversion is not great enough to supply the quantity that is lacking. This case was temporarily met with in the above-mentioned experiment above  $450^{\circ}$ . Above this temperature somewhat too low pressures were namely found, but if the temperature was kept constant for half an hour, a rise of the pressure occurred again.

itself as a designation of the stable solid modification of the phosphorus<sup>1)</sup>.

Messrs. COHEN and OLIE<sup>2)</sup> thought that the violet phosphorus was a simple substance, and that the red phosphorus had to be taken as a solid solution of white phosphorus in violet phosphorus, the concentration of which would be a temperature function, or in other words that the red phosphorus would be a state of internal equilibrium.

It has now, however, appeared most convincingly that this view is erroneous, and that the violet modification of the phosphorus, i.e. the *unary stable* form of the phosphorus, just as the unary metastable form, the white phosphorus, is a state of internal equilibrium, and that what is understood by *red phosphorus* is an *intermediate metastable* state, which is *not in internal equilibrium*.

This intermediate state, which, therefore, does not occur in the unary system, is a state of the pseudo system, and consists of one or more mixed crystals.

That the phosphorus with which Messrs. COHEN and OLIE worked, was no state of internal equilibrium, one of us (SMITS)<sup>3)</sup> demonstrated already before by pointing out that it follows from their experiments that when red phosphorus was brought from higher to lower temperature, the specific gravity was not reduced, though the state of equilibrium at a lower temperature would have to correspond to a smaller specific gravity.

#### 4. *Transition point of the white phosphorus.*

While thus the red phosphorus has disappeared from the unary system of this element, this vacancy has again been filled by BRIDGMAN<sup>4)</sup>, who found lately that the white phosphorus exhibits a transition point at  $-80^{\circ}$ , where the regular white phosphorus assumes a hexagonal form. It follows therefore from this that the phosphorus possesses a metastable transition point.

#### 5. *BRIDGMAN's black phosphorus.*

BRIDGMAN speaks further of *black* phosphorus, which he has obtained by subjecting white phosphorus at  $200^{\circ}$  to a pressure of from 12000

<sup>1)</sup> In our previous communication we thought we had to retain the denomination of *red phosphorus*, but it appeared that this might give rise to all kinds of mistaken ideas.

<sup>2)</sup> Z. f. Phys. Chem. **71**, 1 (1900).

<sup>3)</sup> Z. f. phys. Chem. **76**, 421 (1911).

<sup>4)</sup> Journ. Amer. Chem. Soc. **36**, 1344 (1914).

to 13000 kg. per  $\text{cm}^2$ . When red phosphorus was started from, this black phosphorus did not form, however, under the same circumstances of temperature and pressure. Undoubtedly this difference is owing to the circumstance that the chemical transformation required to obtain the black phosphorus makes its appearance more easily in the strongly metastable liquid than in the much less strongly metastable *intermediate state*, the red phosphorus. At higher temperature also red phosphorus, and also the violet modification, will have to become black.

Whether this black modification is really a new modification is still to be decided.

After BRIDGMAN's publication had come under our notice, we asked him to supply us with a small quantity of his black phosphorus in order to investigate this state further by means of vapour pressure determinations etc. Mr. BRIDGMAN has very kindly complied with this request, and we gladly avail ourselves of this opportunity to render him our best thanks for his kindness.

Amsterdam, 24<sup>th</sup> Dec. 1914.

Anorg. Chem. Laboratory  
of the University.

**Chemistry.** — "*Further particulars concerning the system phosphorus.*"

By Prof. A. SMITS and S. C. BOKHORST. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of December 30, 1914).

1. *The vapour tension formula for the violet phosphorus.*

When calculating the values for  $T \ln P$  from the observed vapour tensions of the solid violet phosphorus (see preceding communication), we find what follows.

When just as we have done for liquid violet phosphorus, we represent  $T \ln P$  graphically as function of  $T$ , we come to the result that as Fig. 1 shows the values for  $T \ln P$  obtained for the preparations 4 and 1 with the exception of the two lowest points, are without any doubt situated practically on a straight line.

That this is not the case with the two lowest points, is of course to be ascribed to an inaccuracy in the experiment. This inaccuracy may be owing to this that during the heating of the phosphorus in the glass spring, when the latter was being evacuated with the GAEBDE pump, a small quantity of white phosphorus was condensed from the vapour on the wall of the glass spring, which of course

TABLE I.  
Preparation 2.

$t$	$T$	$P$	$T \ln P$
290°	563°	0.05 atm.	— 1686.6
308.5	581.5	0.09 "	— 1400.2
328	601	0.15 "	— 1140.2
346	619	0.25 "	— 858.1
365	638	0.39 "	— 600.7
384.5	657.5	0.60 "	— 335.8
410	683	1.02 "	+ 13.5
429	702	1.54 "	+ 303.1
444.5	717.5	2.16 "	+ 552.5
456	729	2.82 "	+ 755.7

TABLE II.  
Preparation 3.

$t$	$T$	$P$	$T \ln P$
308.5	581.5	0.08 atm.	— 1468.7
346	619	0.17 "	— 1096.8
375.5	648.5	0.40 "	— 594.2
394.5	667.5	0.65 "	— 287.5
418	691	1.12 "	+ 78.3
448.5	721.5	2.23 "	+ 578.6
457.5	730.5	2.89 "	+ 775.2
461.5	734.5	3.17 "	+ 847.4
474.5	747.5	4.19 "	+ 1070.9

TABLE III.  
Preparation 4.

308.5	581.5	0.07 atm.	— 1543.1
346	619	0.13 "	— 1263.1
379.5	652.5	0.35 "	— 685.13
408.5	681.5	0.79 "	— 160.67
433.5	706.5	1.49 "	+ 281.79
450.5	723.5	2.30 "	+ 587.64
463.5	736.5	3.18 "	+ 852.20
472.5	745.5	3.88 "	+ 1011.0
486.5	759.5	5.46 "	+ 1289.5

TABLE IV.  
Preparation 1. 1)

$t$	$T$	$P$	$T \ln P$
505°	778°	8.67 atm.	1680.4
515	788	10.43 "	1847.6
522.5	795.5	11.61 "	1950.4
561	834	24.3 "	2661.3
578	851	34.35 "	3009.6
581	854	36.49 "	3071.8
587.5	869.5	41.77 "	3211.5
588	861	42.10 "	3220.1
589	862	42.5 "	3232.1
589.5	862.5	43.1 "	3246.6

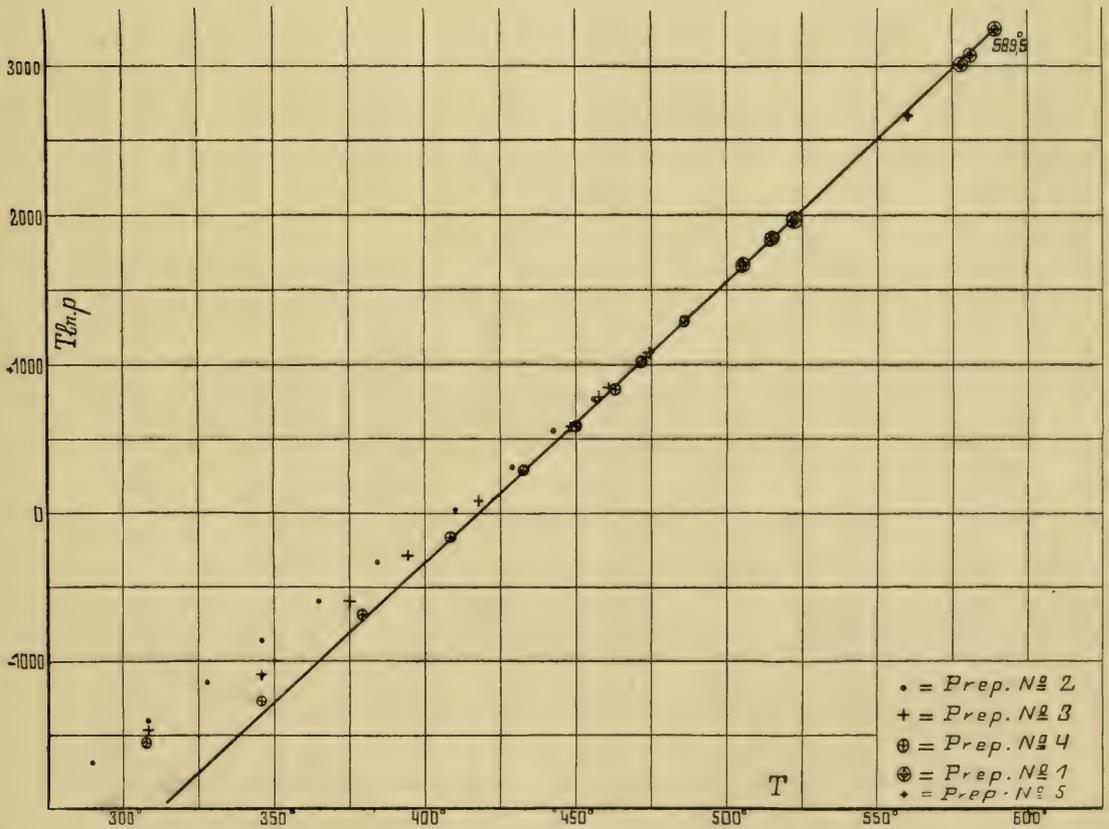


Fig. 1

1) Only the most reliable determinations have been used here. The determination at 561° refers to preparation 5.

gives rise to a too high pressure at the lower temperatures, where the establishment of the internal equilibrium takes place so exceedingly slowly.

Besides it is possible, and this is probably the chief reason, that preparation 4 has not yet entirely assumed internal equilibrium at the temperature of preparation, and that therefore the preparation still contained somewhat too much of the volatile pseudo-component.

This somewhat too much caused at those temperatures at which the internal equilibrium sets in most slowly, the greatest error and this will probably be the reason why the deviations are greatest at the lowest temperatures. Considered from this point of view also the much greater discrepancies which the preparations 2 and 3 exhibit at lower temperatures, can be accounted for in a plausible way.

Hence it follows from our investigation about the vapour tension of the solid violet phosphorus that just as for the liquid violet phosphorus  $T \ln P$  represented as function of  $T$ , yields a straight line, from which it therefore appears that the quantity  $Q$  in the equation:

$$\frac{d \ln p}{dT} = \frac{Q}{RT} \dots \dots \dots (1)$$

may be considered as a constant, so that we get through integration:

$$\ln p = -\frac{Q}{RT} + C \dots \dots \dots (2)$$

or

$$T \ln p = -\frac{Q}{R} + CT \dots \dots \dots (3)$$

As we have also done for the liquid violet phosphorus, we can again find the constant  $C$  graphically also here, as it is equal to the tangent of the angle  $\alpha$ , which the line  $T \ln P$  as function of  $T$  forms with the temperature axis, for:

$$C = \frac{T_2 \ln p_2 - T_1 \ln p_1}{T_2 - T_1} = \operatorname{tga}.$$

We have  $T_1 \ln P_1 = -1400$  for  $T_1 = 343,5^\circ + 273^\circ$ ;  $T_2 \ln P_2 = 3246,6$  for  $T_2 = 589,5^\circ + 273^\circ$ , from which follows  $C = 18,889$ , a value which is about twice the value of the constant for the *liquid* violet phosphorus.

When with this value for  $C$  we now calculate the quantity  $\frac{Q}{R}$  for different temperatures, making use of the tables II and IV, we get what follows:

Temperature	$\frac{Q}{R}$
308°.5	12527
346	12958
.....	.....
379.5	13010
408.5	13034
433.5	13065
450.5	13079
463.5	13060
472.5	13071
486.4	13057
505	13006
515	13037
522.5	13076
(561)	(13092)
578	13065
581	13060
587.5	13043
588	13044
589	13051
589.5	13046
Mean	13050

When we now disregard the two first values, because as the graphical representation shows, they certainly refer to determinations which contain a much greater error than the others, and if we also exclude the determination at 561°, because certainly no internal equilibrium had set in here yet, we get as mean value 13050.

Now that  $C$  and  $\frac{Q}{R}$  are known, we can calculate the pressures for the temperatures at which the preparations 1 and 4 have been investigated. Doing this, we get what follows:

Temperature	Observed pressure	Calculated pressure
308.5	0.07 atm.	0.03 atm.
346	0.13 „	0.11 „
...	...	...
379.5	0.35 „	0.33 „
408.5	0.79 „	0.77 „
433.5	1.49 „	1.52 „
450.5	2.30 „	2.34 „
463.5	3.18 „	3.22 „
472.5	3.88 „	3.99 „
486.5	5.46 „	5.51 „
505	8.67 „	8.29 „
515	10.43 „	10.26 „
522.5	11.61 „	11.98 „
561	(24.2)	25.5 „
578	34.35 „	34.95 „
581	36.49 „	36.90 „
587.5	41.77 „	41.38 „
588	42.10 „	41.77 „
589	42.6 „	42.5 „
589.5	43.1 „	42.9 „

2. *Heat of sublimation, heat of evaporation and heat of melting of the violet phosphorus in connection with the theory of allotropy.*

From the foregoing calculations exceedingly remarkable conclusions may be drawn.

From the value for  $\frac{Q}{R} = 13050$  follows for the mol. heat of sublimation the extraordinarily high value 25.839 K. Cal., while we have found 9.962 K. Cal. for the mol. heat of evaporation of liquid violet phosphorus, so that 15.877 K. Cal. follows from these two quantities for the mol. heat of melting.

According to the theory of allotropy evaporation and melting is accompanied with a chemical reaction between the pseudo components of the substance, and the more the coexisting phases differ in con-

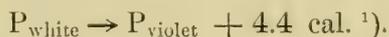
centration, the greater will be the chemical transformation of one phase into another. It follows from this that the sublimation heat, the evaporation heat of the liquid and the melting heat will consist for a greater part of a chemical heat as the coexisting phases differ more in concentration. The quantities of heat found above are of importance in this respect, because they confirm this view in the most convincing way.

According to the theory of allotropy the difference in concentration between the solid violet phosphorus and the vapour is greatest, and that between the liquid phosphorus and the vapour smallest. This tallies perfectly with the colour of the phases; the vapour phase is always colourless, just as the liquid phase.

The evaporation of the solid phosphorus and the melting of the solid phosphorus will therefore be processes which are accompanied with a strong chemical conversion, whereas this reaction is probably only slight during the evaporation of the liquid.

The found values for the three mentioned quantities of heat confirm this perfectly, and the exceedingly high values for the mol. sublimation heat and the mol. melting heat prove that the heat effect is for the greater part a chemical heat. The sublimation heat of the violet phosphorus is even so great that it is of the order of magnitude of the sublimation heat of  $\text{NH}_4\text{Cl}$ , which amounts to 37.9 K. Cal., and in which the dissociation heat is included.

For the difference of energy between white and violet phosphorus per gram-atom the following has been found:



If we now assume for a moment, what certainly is not far from the truth, that this heat effect is entirely a chemical heat, and if we further assume that these two phases differ almost as much from each other in concentration as the violet phosphorus and its vapour, then a chemical heat of about  $4 \times 4.4$  K. Cal. will be included in the mol. sublimation heat. If we subtract this heat effect from the molecular sublimation heat, we keep for the physical heat  $25.8 - 17.6 = 8.2$  K. Cal.; this is a heat effect that lies already much nearer the sublimation heats of other comparable substances in which a chemical heat is also included, but a much smaller one than for the violet phosphorus. The mol. sublimation heat of  $\text{SO}_3$ , e.g. amounts to 11.79 K. Cal.<sup>2)</sup>.

The difference in concentration between violet phosphorus and

<sup>1)</sup> GIRAN, Ann. Chim. phys. (7) 30, 203 (1903).

<sup>2)</sup> C. R. 90, 1511 (1880).

the coexisting colourless liquid phase is certainly considerably smaller than that between violet phosphorus and its vapour, which also follows from the molecular heat of melting, for which we found, as was stated above, 15,877 K. Cal. from the mol. sublimation heat and evaporation heat.

### 3. *Size of the phosphorus molecule.*

As we published some time ago<sup>1)</sup> we succeeded in determining the vapour tension line of liquid phosphorus between 504° and 634°. On that occasion we showed at the same time that when  $T \ln P$  is represented as function of  $T$ , a perfectly straight line is formed as a proof that here too the  $Q$  from the equation:

$$T \ln P = -\frac{Q}{R} + CT$$

is no appreciable function of the temperature.

Now lately WAHL<sup>2)</sup> determined the critical temperature of liquid violet phosphorus in a quartz tube, and found for it the temperature 695°. As now the line for  $T \ln P$  as function of  $T$ , appeared to be a straight line from 504° to 634°, it was perfectly justifiable to prolong this line to 695°, hence to read the value of  $T \ln P$  at  $T = 695^\circ + 273^\circ = 968^\circ$  by extrapolation, and derive from this the value of  $P$ , hence of the critical pressure. In this way 4284 was found for  $T \ln P$ , from which follows  $P_k = 83.56$  atm.

Now that we know the critical data for the liquid violet phosphorus it is of importance to inquire what can be derived from these data about the size of the phosphorus molecule.

For this purpose we calculate the  $b$  value by the aid of VAN DER WAALS' relation:

$$b = \frac{1}{8.273} \cdot \frac{T_k}{P_k} = \frac{1}{8.273} \cdot \frac{268}{83.6}$$

or

$$b = 0,005304.$$

When we now assume the  $b$  to be an additive quantity we can find the  $b$  of a phosphorus atom e.g. from the  $b$ -value of e.g.  $\text{PH}_3$ , and when we then divide the  $b$  value of the phosphorus molecule by this value, we find the number of atoms of phosphorus present in the molecule.

<sup>1)</sup> These Proc. Vol XVI. p. 1174.

<sup>2)</sup> Meddelanden Fran Finska Kemistsamfundet 1913, 3.

For the critical quantities of  $\text{PH}_3$ , LEDUC and SACERDOTE<sup>1)</sup> found what follows:

$$t_k = 52,8^\circ \text{ and } P_k = 64 \text{ atm.}$$

If the  $b$  is calculated from this, we find:

$$b = 0,002330.$$

According to VAN DER WAALS' new views "*The volume of the molecules and the volume of the component atoms*"<sup>2)</sup> hydrogen presents the peculiarity that the  $b$  of a hydrogen atom in a compound is much smaller than in the hydrogen molecule; it amounts viz. to 0.000362 instead of 0.000825, from which follows that for the 3 hydrogen atoms in  $\text{PH}_3$ , 0,001086 must be taken. We then get:

$$0,002330 - 0,001086 = 0,001244$$

for the  $b$ -value of the phosphorus atom, from which follows:

$$\frac{0,005304}{0,001244} = 4,26$$

for the size of the phosphorus molecule at the critical temperature and pressure of the liquid violet phosphorus.

This result already points to a small association, for on an average the phosphorus molecule is greater than  $P_4$ .

4. *Calculation of the factor  $f$  of VAN DER WAALS' vapour tension formula.*

Finally we have also calculated the value of the factor  $f$  from the empirical vapour tension equation of VAN DER WAALS.

$$-\ln \frac{P}{p_k} = f \left( \frac{T_k}{T} - 1 \right)$$

When we consider the pressures at two different temperatures, then it follows from this relation that

$$\frac{0,4343 (T_1 \ln P_1 - T_2 \ln P_2)}{T_1 - T_2} = f,$$

from which it appears that  $f$  is graphically to be derived from the line that represents  $T \ln P$  as function of  $T$ . Over a range of temperature of  $200^\circ$ , viz. from  $500^\circ$  to  $700^\circ$ ,  $T \ln P$  increases from 2388 to 4332, so by 1944.

From this follows that:

$$f = \frac{0,4343 \times 1944}{200} = 4,221.$$

1) C.R. 125, 397 1897).

2) These Proc. Vol. XVI. p. 880.

For substances for which the size of the molecules in the vapour and the liquid phase is equal or about equal  $f$  is about 3, so that the value 4,221 indicates that for the violet phosphorus the average size of the molecules in the coexisting vapour and liquid phases is different.

A discussion of the vapour tension line of the white phosphorus will be reserved for another paper.

*Anorg. Chem. Laboratory of the University.*

*Amsterdam, Dec. 24, 1914.*

**Anatomy.** — *“On the termination of the efferent nerves in plain muscle-cells, and its bearing on the sympathetic (accessory) innervation of the striated muscle-fibre. By Prof. J. BOEKE.*

(Communicated in the meeting of December 30, 1914).

In recent years it has been demonstrated for a large number of different types of striated muscle-fibres of vertebrates, that the motor nerve-endings, which carry the nervous impulses towards the muscular fibres, are hypolemmal in position, i.e. are not lying outside the sarcolemma of the muscle-fibres as maintained by most of the earlier observers, but pass through the sarcolemma, which becomes continuous with the neurilemma, penetrate into the sarcoplasm of the muscle-fibre, which is considerably thickened as the site of formation of the end-organs, and it was further assumed, that here the neuro-fibrillar expansion of the motor nerve-ending is directly continuous with a reticulum in the sarcoplasm, the so-called “periterminal network”<sup>1)</sup>.

At the same time it was shown, that beside the common motor nerve-ending there must be distinguished another afferent nerve-ending on the striated muscle-fibres of vertebrates, which may either be found imbedded in the same granular bed of sarcoplasm or “sole” of the motor endorgan of KÜHNE, or reaching the muscle-fibre independent of this, but always having a hypolemmal position in the muscle-fibre<sup>2)</sup>. This “accessory” nerve-ending is always found at the end of a non-medullated nerve-fibre. As it could be shown, that these accessory nerve-endings did not degenerate after the cutting of the efferent muscle-nerve near the place of exit from the central nervous system, before the entering of the sympathetic nerve-fibres

<sup>1)</sup> J. BOEKE. Beiträge zur Kenntniss der motorischen Nervenendigungen. I. II. Internat. Monatschr. f. Anatomie und Physiologie Bd. 28. 1911.

<sup>2)</sup> J. BOEKE. Die doppelte (motorische und sympathetisch) efferente Innervation der quergestreiften Muskelfasern. Anat. Anzeiger. 44. Band. 1913.

(for example the accessory nerve-endings of the eye-muscle after the cutting of the nervus trochlearis near the mid-brain) which causes the motor nerve-endings of KÜHNLE to degenerate, there was room for the conclusion, that the accessory nerve-fibres and their endorgans were of sympathetic origin, and perhaps had something to do with the tonic innervation of the striated muscle<sup>1)</sup>. In my first paper, which dealt with these nerve-fibres (Congress Utrecht, April 1909), this conclusion was already drawn by me<sup>2)</sup>. In the years 1913 and 1914 strong supporting evidence has been given to it by the admirable physiological experiments of DE BOER<sup>3)</sup>.

In Fig. 1 is shown a degenerated motor nerve-ending (*m*) in a

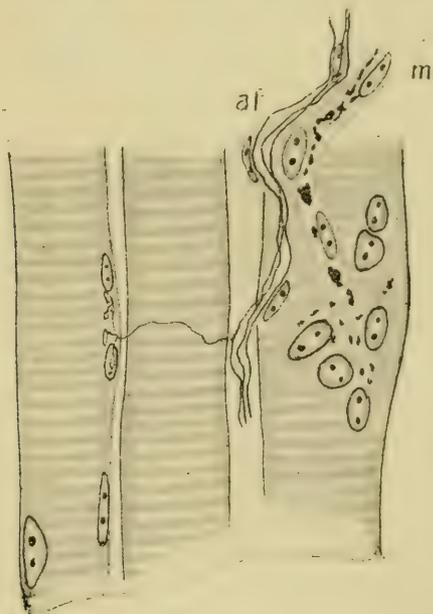


Fig. 1.

Nerve-endings in muscle-fibres of the musc. obl. sup. oculi of the cat,  $3\frac{1}{2}$  days after section of the nervus trochlearis.

*af* = accessory (sympathetic) fibre with end-organ, not degenerated.

*m* = degenerated motor nerve-fibre with degenerated end-organ.

muscle-fibre of the superior oblique muscle of the eye-ball of a cat some days after section of the nervus trochlearis near the mid-brain. The accessory non-medullated nerve-fibre (*af*) is not degenerated.

<sup>1)</sup> See note 2, p. 982.

<sup>2)</sup> Proceedings of the 9th phys. and medical Congress. Utrecht, April 1909. See also the more detailed description in the Anat. Anzeiger 44. Band, 1913.

<sup>3)</sup> S. DE BOER. Folia Neuro-biologica 1913 and 1914.

and shows a normal hypolemmal nerve-ending in a muscle-fibre at the end of one of the non-medullated nerve-fibres.

If thus we may assume this so called accessory innervating apparatus of the striated muscle-fibres to be of a sympathetic (parasympathetic) nature, then the following question arises immediately: both the motor nerve-ending and the accessory nerve-endings are hypolemmal in position, i.e. the nerve-fibre passes through the sarcolemma and enters the muscle-fibre, being imbedded in the granular substance of the sarcoplasm, and directly continuous with the intraprotoplasmatic reticulum of the periterminal network. Now it is generally assumed, that the efferent sympathetic nerve-endings do *not enter* the plain muscle-cells, but terminate by tapered or bulbous extremities which are applied to the outer surface of the cells. Why should there exist such a curious contradiction between equivalent elements? Why should the accessory nerve-ending in the voluntary muscle-fibres (when of sympathetic origin) be hypolemmal, and the sympathetic nerve-ending in plain muscle-cells remain on the outside of the innervated elements? We will try to show, that there is no such contradiction, and that the efferent nerve-endings in plain muscle-cells have exactly the same position as the accessory nerve-endings, which give the striated muscle-fibres their tonic impulses.

In general the modes of termination of the efferent nerves in involuntary muscles are rather difficult to study. The Golgi-method and staining with methylene blue often procure splendid results, but these methods do not allow to give a definite answer as to the exact relations between the nerve-endings and the plain muscle-cells. Apart from earlier aberrant accounts, that localised the terminations of the nerve-fibres inside the cell, even inside the nucleus and the nucleolus (THANHOFFER, lastly OBREGIA in 1890), all the observers agree (I need only mention the names of KÖLLIKER, LÖWIT, ERIC MÜLLER, HUBER and DE WITT, S. RETZIUS), that the efferent nerves of the plain muscle-cells form complicated plexuses between the elements of the involuntary muscular tissue, in which the nerve-fibres bifurcate and give off branches at frequent intervals, and then, either united with those from adjoining nerve-fibres or not, come into close relation with the plain muscle-cells themselves, either terminating by tapered or bulbous extremities which are applied to the surfaces of the cells, or ending in networks and loops, without having free extremities.

Thus even the last observer in this field, AGABABOW<sup>1)</sup>, who studied

<sup>1)</sup> A. AGABABOW. Ueber die Nerven der Augenhäuten, v. Graefe's Archiv für Ophthalmologie, 83. Bnd, 2. Heft. 1912,

J. BOEKE: "On the termination of the afferent nerves in plain muscle-cells, and its bearing on the sympathetic (accessory) innervation of the striated muscle-fibre."



Fig. 2.

Terminations of the different nerves of the Musculus Ciliaris of the human eye.

*ab* = sensory terminal buds.

*c* = neurofibrillar network between the musclecells.

*d-h* = efferent motor intracellular endings.



the distribution and mode of termination of the nerve-fibres in the corpus ciliare and the adjacent membranes of the human eyeball, states, that "in keinem einzigen seiner Praeparate je etwas zu sehen war, was als ein unmittelbarer Zusammenhang des Nerven-fädchens mit dem Protoplasma, dem Kern oder gar dem Nucleolus der Muskelzellen zu deuten wäre"<sup>1)</sup>.

AGABABOW, as I mentioned before, studied the innervation of the corpus ciliare. This led him chiefly to a confirmation of his earlier observations on the same subject in the year 1897. In the corpus ciliare of human eyes and of the eyeballs of albinotic cats AGABABOW demonstrated the presence of the following nerve-terminations: 1. endorgans of the motor nerves in the plain muscle-cells of the musculus ciliaris, 2. vasomotor nerves for the ciliary bloodvessels, 3. terminations of afferent sensory nerves in the corpus ciliare, 4. terminations of afferent nerves in the lamina suprachorioidea, which covers the corpus ciliare as a loose soft membrane of areolar connective tissue at the outside. As for the motor nerves of the musculus ciliaris, they appeared in his preparations of cats' and mens' eyes (Golgi- and methylene blue-preparations) as numerous fine varicose threads running between the muscle-cells; at different points, always outside the cell-boundary, the nerve-fibres terminate and the ends are applied to the cell-surface. This however is after the observations of AGABABOW not yet the real ending of the nerve-fibres, for sometimes he could see one of these delicate fibres bifurcate again and the two exceedingly delicate terminal branches could be followed around the muscle-cell, encircling it on both sides. From these observations AGABABOW draws the conclusion<sup>2)</sup>: "dass eine jede Muskelzelle von einem Netze sehr feiner Nervenfäden umflochten wird; hierbei stehen die Nervenetze der Nachbarzellen noch durch 2—3 Fädchen unter einander in Verbindung. Diese Endigungsart der motorischen Nerven in Gestalt eines perizellulären Netzes, welches eine jede Muskelzelle umspinnt (ohne terminale Anschwellungen) ist mit grosser Wahrscheinlichkeit eine für die motorischen Nerven der glatten Muskulatur (Sphincter iridis, Gefässe, Darm) allgemeine Erscheinung".

AGABABOW studied the innervation of the corpus ciliare by means of the Golgi-method and intra-vitam staining with methylene blue. Now this account of AGABABOW coincides entirely with what I have seen in a number of Golgi- and methylene blue preparations of the

<sup>1)</sup> l. c. p. 355.

<sup>2)</sup> l. c. p. 358. cf. TIMOFEJEV 1896.

muscular coat of the intestine and of bloodvessels. The pictures only vary on account of the presence or of the distribution and number of the so-called terminal buds. Preparations after these methods are not sufficient however to study the intrinsic relations between nerve-endings and muscle-cells. For this we need thin (5—10  $\mu$ ) serial sections of material sharply stained after the neurofibrillar staining-methods of CAJAL or BIELSCHOWSKY and counterstained by Haematoxylin and Eosin or Orange G. Unfortunately these staining-methods generally give only mediocre results, when applied to involuntary muscle-cells, and even in the best preparations the nervous plexuses between the muscular elements may be stained very sharply, but generally the final terminations are either not stained at all or take such a light stain, that it is impossible to draw any conclusions about the real relations between the nervous and muscular elements from them.

Some time ago however I got at my disposal, thanks to the kindness of Prof. P. TH. KAN, the director of the oto-laryngological section of the academic Hospital of our University, a freshly-enucleated normal human eye, which immediately after having been enucleated, had been put into a large quantity of neutral formaline-solution of 12 %.

Parts of the corpus ciliare and iris of this object were treated by the method of BIELSCHOWSKY, and these preparations turned out to have taken such a splendid stain as I had never yet met with in any of my neurofibrillar preparations of plain muscle-cells. Beside a very good preservation of the different histological elements the sections showed a perfect and strong colouring of the nervous elements, of which even the finest terminal fibrils and endings were visible as extremely delicate black lines, the thinnest of which were scarcely visible except under the highest power, but still stained a dark brown.

In this object I studied the relations between the nervous elements and the muscle-cells of the corpus ciliare. Serial sections (4—20  $\mu$ ) were made through the corpus ciliare and iris in a transverse or a tangential direction. As a counterstain for the nuclei and the protoplasm were used haematoxylin and eosin or orange G. Especially the tangential sections through the musculus ciliaris were very instructive.

Letting alone for the moment the sensory innervation of the surrounding tissues, which need not be described here, we find, on turning our attention to the musculus ciliaris, two different systems of nervous terminations between the muscle cells. In the first place a

loose plexus (at places perhaps a network) with wide meshes of nervous non-medullated or partly medullated fibres, that end in distinct sheathed bulbous or coiled-up terminations; some of these are shown in fig. 2 (*a* and *b*). Since these nerve-fibres and their terminations lie in the connective-tissue around bundles of the plain muscle-cells and remain entirely independent of the muscle-cells, they must be regarded as the free nerve-endings of sensory nerves, which are already described by AGABABOW as being distributed in large numbers throughout the whole of the corpus ciliare.

In the second place we see in the musculus ciliaris a very fine plexus and network of very fine non-medullated nerve-fibres, with small meshes, lying between the muscle-cells, which at first sight seems to be of a bewildering complexity. Only gradually one learns to find one's way in the mass of extremely delicate black-stained threads running to and fro between the muscle-cells, and then it becomes clear, that this plexus contains in the first place the network described by AGABABOW, consisting of fine varicose nerve-threads, running between the muscle-cells, surrounding these cells, encircling them with smaller and longer meshes of extremely delicate fibrils and more or less thickened points of junction. At these points, visible in methylene blue-preparations as knots of a homogeneous blue colour, the neurofibrillar apparatus appears, when studied under the highest power, to be broken up into an extremely fine network of fibrillae. In fig. 2 at *c* a mesh of this network, magnified 2100 diameters is drawn. This network is the terminal network of AGABABOW. But now a close study of the sections soon reveals the fact, that this network, which encircles the muscle-cells, is *not* the terminal nervous apparatus. From the nerve-threads composing the meshes of this network, lying between the muscular elements and encircling them, are branched off at all points extremely delicate neurofibrillae, fine filaments having only a diameter of several millimicra, but appearing, thanks to the splendid impregnation of the sections, as distinctly visible black-stained threads of the greatest tenuity. Only these threads, that form a second network or plexus, exhibit the ring-shaped varicosities, the end-rings and small terminal nets, which must be regarded as the real terminations of the nervous apparatus. Some of these end-rings are drawn from the sections in fig. 2, *d—f*. But the fact, which interests us chiefly here, is that these end-rings (the termination of these final nervous branches is chiefly in the form of small rings or loops) are found lying *intraprotoplasmically* inside the muscle-cells, and the fine fibrillae, composing this second network, form a reticulum in the protoplasm of the muscle-cells, encircling

the nucleus, running between the myofibrillae of the cell, and thus showing their intracellular position, finally giving off branches, that are so exceedingly fine and form such small meshes, that they cannot be distinguished from the protoplasmatic reticulum of the cytoplasm of the muscle-cells itself. Indeed, one gets the impression, that these finest terminal branches, given off by the delicate threads of the intraprotoplasmatic neurofibrillar reticulum, described above, are in the end nothing else but the protoplasmatic reticulum.

That this intraprotoplasmatic neurofibrillar reticulum with its ring-shaped varicosities and end-rings or terminal nets at the end of short twigs in reality lies inside the cell in the cytoplasm and not applied to the surface at the outside of the cell, may be demonstrated in the first place by the following fact. The muscle-cells of the musculus ciliaris are not always compact, but especially in the inner part more loosely arranged, so that in tangential sections through the inner parts of the corpus ciliare one often sees muscle-cells lying entirely isolated in the connective tissue. In these cases it is easy to determine whether the second neurofibrillar reticulum, mentioned above, lies inside the cytoplasm of the muscle-cell or simply surrounds the cell at the outside, and the intraprotoplasmatic position of this second reticulum with its ring-shaped varicosities and end-rings, together with the very delicate threads passing from this network into the protoplasmatic reticulum could be established with accuracy. Still, there is room for doubt, for a bundle of two muscle-cells might be cut lengthwise and it might be possible, that what was thought to lie in the cytoplasm, in reality was lying just between the two muscle-cells.

But the conclusion that the terminal branches of the neurofibrillar apparatus together with the terminal rings are intraprotoplasmatic in position is placed on a perfectly sure basis, when cases are found as are figured in fig. 2 *g* and *h*. Here we see the small terminal rings and nets of the second neurofibrillar network lying so close to the nucleus of the muscle-cell, that they even make an indentation into the nucleus, and thus are found lying in a shallow hole in the side or on the top of the elongated nucleus (fig. 2 *g* and *h*). Such cases are not rare in my preparations, indeed in nearly every section through the musculus ciliaris were found one or two of them; they can only be explained by adopting an intraprotoplasmatic position for the neurofibrillar rings. In many of these cases the connection of the rings, lying in the indentation of the nucleus, with the neurofibrillar network could be observed with perfect accuracy, and in several cases the direct connection of this intraprotoplasmatic neuro-

fibrillar network with the network lying between the muscle-cells on one side, with an exceedingly fine protoplasmatic reticulum on the other side, losing itself in the cytoplasm, could be seen with great clearness.

Thus the apparent controversy between the relations of the accessory nerve-terminations and the striated muscle-fibres on the one hand, of the sympathetic nerve-terminations and the plain muscle-cells on the other hand, is seen to disappear. In the plain muscle-cells we find the same identical relations of nerve-endings and sarcoplasm as in the striated muscle-fibres. In both elements the neurofibrillar apparatus penetrates into the protoplasmatic (sarcoplasmatic) cell-body, forms the terminal nerve-endings inside the cell-body as small end-rings and loose netlike extremities or varicosities, and is in continuous connection with a very delicate protoplasmatic (or intraprotoplasmatic) reticulum, the periterminal network.

*Leiden, December 1914.*

**Anatomy.** — “*On the mode of attachment of the muscular fibre to its tendonfibres in the striated muscles of the vertebrates.*”

By Prof. J. BOEKE.

(Communicated in the meeting of December 30, 1914).

Where the cross-striated musclefibres end in a tendon, the tendon becomes subdivided into as many small bundles as there are fibres in the end of the muscle, and each separate musclefibre has its separate small bundle of tendonfibrillae, to which it is attached. It often seems at first sight as if the tendon-fibres are directly continued into the muscular substance, but until recently it was generally admitted, that the fibres of each tendon-bundle ended abruptly on reaching the rounded or obliquely truncated often somewhat swollen extremity of a muscular fibre, and are only so intimately united to the prolongation of sarcolemma which covers the rounded extremity of the muscular fibre entirely, as to render the separation of the two difficult if not impossible, while the muscular substance, on the other hand, may readily be caused to retract from the sarcolemma at this point as at other points of its course.

While thus it was until recently generally admitted, that the extremity of a muscle fibre was covered entirely by the uninterrupted sarcolemmal membrane, in the year 1912 O. SCHULTZE<sup>1)</sup> and after him several of his pupils published the results of observations of a

<sup>1)</sup> O. SCHULTZE. Ueber den direkten Zusammenhang von Muskelfibrillen und Sehnenfibrillen. Arch. f. Mikrosk. Anatomie. Bd. 79. 1912. pag. 307–331.

different nature, viz. that at the supposed end of the muscle fibres, where the fibres are attached to the tendon, the myofibrillae are directly continued into the tendon-fibres and the sarcolemma is not closed at the extremity of the muscle fibres, but perforated by the myofibrillae, these being directly continuous with the fibrillae of the tendon. According to these statements we should find in the striated muscles the curious disposition, that protoplasmatic, strongly differentiated, *intracellular* fibrillae, the myofibrillae, would be directly continuous with collagenous connective tissue-fibrillae, which are formed *extracellularly* by special connective-tissue cells, the fibroblasts.

It is easily understood, that such an opinion would not remain uncontradicted, and thus the publication of the paper by SCHULTZE mentioned above has called into life already a pretty large number of papers on the same subject; and indeed, one should think twice before joining in a strife about such a difficult problem, and which is not always conducted with the impartiality and courtesy held so high in scientific discussions. And the writer of the present paper surely would not have entered the arena, if it were not, that his observations, which are recorded in the present paper, according to his opinion, are apt to show, that in both statements there is an element of truth, as far as the observations go, made by SCHULTZE and his opponents in their preparations of adult muscle fibres — though the line must be drawn here, and in reality the truth seems to lie not in the middle, but on the side of the opponents of SCHULTZE, the interpretation of his observations being wrong.

Undoubtedly longitudinal sections of adult musclefibres often seem to show a mode of attachment to the tendon-fibres corresponding exactly with the drawings and statements made by SCHULTZE and his followers, and when studying a great number of well-preserved and well-stained sections of muscle- and tendonfibres, as I did in the course of the last ten years<sup>1)</sup>, one is often tempted to doubt the truth of the theory of the discontinuity of the muscle- and tendon-fibres and the closed appearance of the sarcolemma at the extremity of the muscle-fibres.

Again and again one tries to find the boundary line of the sarcolemma without getting definite results, and surely the paper by SCHULTZE would have been hailed as containing the long sought-for solution of this histological problem, were it not that the study

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<sup>1)</sup> Even as long ago as 1901 I made a series of sections through the musculature of small salmonidae, which seemed to show with exquisite clearness the direct continuity of muscle- and tendon-fibrillae.

of the ontogenetic development of the muscle-fibres always brought me back to the old, time-honoured theory.

But I must add immediately that even for the adult muscle-fibres the study of the admirable preparations made by Miss Dr. M. VAN HERWERDEN, which she had the kindness to show me in my laboratory, left no doubt as to the truth of her observations against the statements made by SCHULTZE and his pupils. Both the sharply-stained extremely thin sections and the preparations in which the muscular fiber was digested by means of a trypsin-solution<sup>1)</sup>, the sarcolemma and the tendonfibres however left intact, demonstrated very clearly the discontinuity of the elements in question.

It seems to me, that the solution of this problem is given by the ontogenic development of the muscle-fibres, and even here the minute details are not always sufficiently clear to give a definite account of the development of the muscle-cells in relation to their mode of attachment to the tendon-fibrillae.

Splendid material to work with in this direction is given by the developing myomeres, the trunkmyotomes of several teleostians, and especially in *muraenoids* the details of the developmental processes are shown with the utmost clearness. Of muraenoid eggs and larvae, preserved after the best methods, and cut into thin (4—6  $\mu$ ) longitudinal and transverse sections, stained with iron-haematoxylin and counterstained by eosine, our laboratory possesses a large collection of more than a hundred specimens, and at the hand of this series of preparations I will give here an account of the development of the muscle-fibres of the trunk-myotomes.

The general development of the trunkmyotomes, the changes in form and size, the differentiation of the muscle-cells, have been described very fully and illustrated by a large number of drawings in the inaugural dissertation of Dr. A. SUNIER<sup>2)</sup>, so I need not enter into these details here. The first evidences of muscular differentiation consist of the lengthening of the cells of the myotome, until they reach from one end of the myotome, the cranial end, well into the mass of cells toward the other end. The nuclei of these cells alter their staining reaction and begin to divide amitotically,

<sup>1)</sup> The opposite results, obtained by SCHULTZE in his digesting experiments, are, as Dr. VAN HERWERDEN tells me, due to his having used an alkaline solution of trypsin and not the neutral one, he should have used to leave the collagenous fibres intact.

<sup>2)</sup> A. J. L. SUNIER. Les premiers stades de la différenciation interne du myotome et la formation des éléments sclérotomatiques chez les acraniens, les sélaciens, et les téléostéens. Inaug. Dis. Groningen. Brill, Leiden 1911. Has been published also in the Tijdschrift der Nederl. Dierkundige Vereeniging Jaarg. 1911.

at a rate which greatly increases the number of nuclei without dividing the cell body. This latter grows longer until it reaches from the anterior to the posterior boundary of the myotome, while its numerous nuclei are stretched in a single row (in a sagittal section through the body of the larva) from one end to the other. The cells have changed from mononucleated embryonic cells into the elongated and multinucleated *sarcoblasts*.

In these sarcoblasts the muscle fibrillae, the myofibrillae, now begin to appear in the protoplasm. At this stage each sarcoblast appears as a flat, multinucleated, plate-like cellbody, surrounded on all sides by a very delicate but clearly defined thin membrane, the sarcolemma. In each myotome these flat, plate-like sarcoblasts are arranged very regularly in a row as the leaves of a book, so that their broad sides are lying in the frontal plane of the body. They all reach from one end of the myotome through its whole length to the other boundary of the myotome. At the end of the myotome the rows of the thin rounded edges of the muscleplates nearly touch the homologous extremities of the sarcoblasts of the foregoing or following myotome.

When we now study these boundary-surfaces between the myotomes, where the connective-tissue myoseptum is found in older forms and in the full-grown leptocephali, in thin sagittal sections through the larval body, in which sections therefore the sarcoblasts are cut longitudinally and at right angles to the broad surface of the plate-like cellbody, it is always the same sort of picture we get to view. The protoplasmatic<sup>1)</sup> cellbodies of the sarcoblasts, appearing, when cut in the direction mentioned above, as long regular rod-shaped elements, are separated from each other by very thin but clearly defined boundary-lines, running exactly parallel to each other, and at the extremity of the myotome these boundary-lines follow the rounded ends of the sarcoblast in an extremely regular curve, which runs very clearly and distinctly around the entire end of the sarcoblast. There is no interruption of this boundary-line whatever to be seen. Thus all the sarcoblasts of the two myotomes in question are standing with their rounded and perfectly isolated endings in two opposite rows, and they are generally arranged in such a manner, that the ends of the sarcoblasts of one row alternate with those of the sarcoblasts of the other row, belonging to the second myotome, and thus the space between the two rows of sarcoblasts is reduced to a minimum; in this space in a later period of development the

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<sup>1)</sup> Before the appearance of the myofibrillae.

myoseptum is formed. In the developmental stage, which we are studying now, this myoseptum is already to be seen as an extremely thin (0,5—1  $\mu$ ) layer of a homogeneous gelatinous substance (*not* an effect of shrinkage of the elements in the sections), that fills up entirely the room between the two opposite rows of sarcoblastendings.

This homogeneous layer or film of gelatinous substance remains in the same form and conditions throughout the whole of the forelarval period. It is only at the end of this first period of development, when the yolk is nearly absorbed and the small forelarvae begin to migrate towards the bottom of the sea and to grow out to leptocephali, that the formation of tendon fibrillae sets in.

The next step in the differentiation of the sarcoblasts consists of the formation of the striated myofibrillae in the cytoplasm.

I will not enter here into details about the relations between the mitochondria and the myofibrillae and about the first signs of cytoplasmatic differentiation, and only mention here, that we find the first traces of myofibrillar differentiation in the cytoplasm of the sarcoblasts near the extremity of the cell-bodies. And here we meet with an important phenomenon, which in the end, as we shall see later on, gives us the clue to the understanding of the most important facts of the myofibrillar differentiation and the solution of the problem of the union of the tendon- and muscle-fibrillae, which was the starting-point of the present paper, viz. that, as the first traces of the myofibrillae appear as small dots or rods, stained black by the iron-haematoxylin, in the two rows of sarcoblast-ends of two different myotomes, separated by the thin layer of gelatinous substance of the primitive myoseptum, these dots or rods are lying exactly opposite to each other in the protoplasm of the two sets of sarcoblasts.

In the developmental stages following the one described here, we find the myofibrillae as long delicate threads, showing the typical cross striation, and running parallel to each other straight from one end of the sarcoblast to the other, congregated into two distinct bundles, thin and flat, leaving a narrow median band of cytoplasm between, in which the nuclei lie imbedded in the protoplasm. By a longitudinal splitting of the myofibrillae and later on of the small bundles, new systems of fibrils are formed<sup>1)</sup>, and this accumulation of fibrils is continued until each sarcoblast seems to be a mass of fibrils with a central median thin layer of sarcoplasm containing the nuclei. In the course of this accumulation-process the extremities of the sarcoblast lining the myoseptum get broader and flatten

<sup>1)</sup> This process is described very fully in the paper by Dr. SUNIER mentioned above.

against the latter, but they still show the same regular outlines. The closer study of these extremities of the muscle-plates lining the myoseptum, always in thin sagittal or frontal sections through the larval body, brings out the following facts. In the first place, as mentioned above, the outline of the extremity of the sarcoblast remains as clearly defined as before, although now the sarcoblast has lost its regular curved outline, but is flattened and broader. The extremely delicate boundary-line of the sarcoblast (we may speak here already of the sarcolemma) is everywhere to be followed with great precision around the entire extremity of the musclefibre.

In the second place, even when a large number of myofibrillae has been accumulated inside the cellbodies of the sarcoblasts, the extremities of these myofibrillae where they touch the sarcolemma, stand in the two rows of muscle-plates lining the thin layer of the primitive myoseptum, always individually exactly opposite each other, in this way, that if we follow the line of a fibril of one of the muscle-plates through the septum into the opposite muscle-plate, we are certain to touch a fibril there with, I should say, mathematical certainty.

As was mentioned above, the myofibrillae arrange themselves inside the cell-body of the muscle plates into two flat bundles, leaving a median layer of undifferentiated sarcoplasm between them containing the nuclei. But at the extremities of the muscleplates lining the myoseptum the ends of the myofibrillae touching the sarcolemma are distributed very regularly over the whole extent of the rounded endline of the muscleplates. To attain this regular distribution the myofibrillae of the two plate-like bundles have to curve round a little at their ends before reaching the sarcolemma, and it is even by this fact, that is shown the accuracy with which nature strives to place the ends of two opposite fibrils exactly in one line. When we prolong the line of such a fibrilla, softly curving round to reach the middle of the extremity of the muscleplate, in the same direction we are certain to touch with the selfsame curve a myofibrilla of the opposite muscle-plate. It is easily understood, that only in this manner a regular distribution of the contracting forces and a correct cooperation of the contracting forces of the contiguous muscle-plates of two myotomes is attained.

From a histogenetic point of view I would explain it in the following manner, without venturing too far out upon the unfamiliar ground of physical theories; we must assume that through the dividing layers of sarcolemma and myoseptum (in this stage of development only an exceedingly thin layer of gelatinous substance,

less than  $1 \mu$  thick) the protoplasts of two opposite muscle-plates exert an influence on each other, in this way that the differentiation of the contractile elements sets in at corresponding points at the surface (the inside of the sarcolemma) or near it, and so the myofibrillae of one muscle-plate have corresponding fibrils in the opposite cells, lying exactly in the same line. But what is the nature of this influence cannot be discussed here.

Thus we see that the myofibrillae can be traced to the sarcolemma, but not beyond it, and that every fibril of a given muscle-plate has a fibril corresponding to it and lying in the same line in the adjacent myotome.

In the stage of development following on the one just described, the larva greatly increases in length, and with this the myotomes lengthen considerably. The myofibrillae inside the muscle plates still extend from one extremity of the cell to the other, and so follow the extension of the myotomes.<sup>1)</sup> Now this longitudinal growth of the myofibrillae does not take place along the whole fibre, but only at two points near the ends. There where the cross striation of the muscle fibre has been fully developed, a further lengthening of the fibril is not possible any more; we never see any signs of a division of the anisotropic or isotropic portions of the striated sarcous segments, the pattern of striation is always the same in all the muscle fibres of the different myotomes, and the breadth of the sarcous segments is always of the same order. But when we study the muscle fibre closely along its whole course, we see that in this larval stage the striation of the myofibrillae does not extend to the extremity of the muscle fibre, but ends abruptly (for all the myofibrillae of a given muscle fibre at the same point) at some distance from the end. Here the myofibrillae of the same bundle are more or less fused together, thickened and so a sort of intercalated knot is formed, which takes a strong black stain when stained with iron-haematoxylin; at this point of the myofibrillae we must locate the lengthening, the longitudinal growth of the entire fibril. From this point onwards to the place of attachment of the fibrillae to the sarcolemma, a distance of about  $10-4 \mu$ , there is no trace of a striation visible; the individual myofibrillae are again separated, attach themselves at different points to the sarcolemma, and here the fibrillae take a somewhat lighter stain than in the striated part of the fibre, and a stain which more or less resembles the colour of the collagenous connective tissue fibrils of a later period of develop-

<sup>1)</sup> In his paper mentioned above, Dr. SUNIER gives many drawings, which show several details of the process of differentiation of the myofibrillae.

ment. Probably it has a slightly altered chemical constitution, and may be regarded as having not a contractile but only a mechanical function and therefore representing to a certain extent a sort of intracellular tendon-fibril. This noncontractile part of the myofibril is formed as a differentiation of the extremity of the myofibrilla, is therefore entirely continuous with the striated part of it, is lying completely intracellular, inside the sarcolemma and attached to it at its end. It is this relation between apparently different sorts of fibrils which is visible in many of the figures of the paper by SCHULTZE mentioned above. According to the mode of development described here, one is not entitled to draw from it the conclusions SCHULTZE and his followers draw from their preparations.

Until now we had to do only with the intracellular fibrillar differentiations. But at this point begins the second phase of the development of the muscle-fibres, the forming of the tendon-fibrillae.

The thin layer of homogeneous gelatinous substance of the primitive myoseptum between the myotomes begins to thicken, connective-tissue cells lying between the epithelium and the myotome begin to migrate slowly in between the myotomes and so step by step the connective-tissue septum of the leptocephali is built up. Afterwards these cells of the secondary myoseptum send cells down between the muscle plates into the myotome, later on blood capillaries follow, and so gradually the features of the adult myotomes are laid down. Even at the first thickening of the primitive myoseptum the differentiation sets in which interests us here most of all, viz. the forming of the tendonfibrillae, a fibrillisation of the substance of the myoseptum, whether under the influence of immigrating connective tissue-cells or directly under the influence of the growing and expanding myotomes is not to be determined. The fact that interests us chiefly here is that in the process of formation of these primary tendon-fibrillae essentially the same features are shown as in the formation of the myofibrillae in the adjacent myotomes. Here likewise we see the fibrillae, the homologa of the collagenous fibrillae of the connective-tissue myoseptum of older forms, differentiated in direct connection with the ends of the myofibrillae of the muscle-plates of the adjacent myotomes. Exactly at the point, where inside the sarcolemma (which is still visible with the same clearness around the extremity of the muscle fibre as before) a myofibrilla is attached to it, a tendon-fibrilla appears attached to the outside of the sarcolemma. And at whatever point we study the differentiation of the tendon-fibrillae, whether in the regular clearly defined myoseptum between the two rows of parallel and close standing muscle-cells of the adjacent

myotomes, or at those points of the larval body, where (as is the case with the muscular differentiations in the head and neck region of the larvae) the muscular elements are arranged more loosely and less regularly, and, instead of being closely packed together as is the case in the myotomes, often end separately or in small bundles in the connective tissue, everywhere we see the formation of the connective tissue fibrils, the tendonfibrils, established in such a manner that the tendon-fibrils are formed in direct connection with the myofibrillae, but outside the sarcolemma.

Thus the investigation of the phenomena of muscular differentiation in the muraenoid larva shows us the following picture of the connection between muscle fibre and tendonfibrils: inside the muscle fibre striated myofibrillae running through the entire length of the fibre, but losing their striation at a small distance of the end, and being attached to the inside of the sarcolemma at the end of the muscle fibre as a homogeneous fibril bearing some resemblance to a tendon fibril. Then follows the delicate line of the sarcolemma running around the extremity of the muscle fibre, to which are inserted the homogeneous ends of the myofibrillae; outside the sarcolemma, attached to it at exactly the same points where the myofibrillae are inserted, appear the tendonfibrillae, running at first in exactly the same direction as the myofibril with which they are connected. Thus there is established a continuity, but not in the sense of SCHULTZE.

But it is easy to understand, that as soon as the myofibrillae accumulate to such numbers as to fill up nearly the entire cell body, it will become extremely difficult to follow the delicate line of the sarcolemma between those bundles of fibrils lying as close together. And then it is we get the pictures drawn by SCHULTZE in his figures and known to us from many a preparation, in which the sarcolemma is clearly defined where there are no myofibrils and only sarcoplasm is present, but in which at those points, where close bundles of myofibrillae attain the end of the muscle fibre, no dividing boundary-line of sarcolemma is to be seen between those bundles and the tendonfibrils lying in the same plane and running in the same direction. This is the continuity which in the figures of SCHULTZE is so conspicuous and seems to be so conclusive. I hope I have been able to demonstrate that at least in the case I have studied, it is only an apparent, not a real continuity.

The observations of SCHULTZE are right, his deductions from these must be regarded with true scepticism, and the conclusions drawn by Dr. VAN HERWERDEN from her trypsin-digestion-preparations, and declared by SCHULTZE to be wrong, are, when viewed in the light

of the ontogenetic development of these structures laid down here, entirely right and founded on facts.

A direct continuity between myofibrillae and tendon-fibrillae in the sense of SCHULTZE does not exist.

*Leiden, December 1914.*

**Physics.** — “On the field of a single centre in EINSTEIN’s theory of gravitation.” By J. DROSTE. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of December 30, 1914).

1. The equations which determine the field of gravitation in EINSTEIN and GROSSMANN’s theory <sup>1)</sup>, are not linear, hence the field corresponding to the tensor  $\mathfrak{T}_{\sigma\nu}^{(1)} + \mathfrak{T}_{\sigma\nu}^{(2)}$  ( $\sigma, \nu = 1, 2, 3, 4$ ) is not the sum of the fields corresponding to the tensors  $\mathfrak{T}_{\sigma\nu}^{(1)}$  and  $\mathfrak{T}_{\sigma\nu}^{(2)}$ . The equations, indeed, present a certain homogeneity; when all the  $g$ ’s are multiplied by the constant factor  $\lambda$  and the  $\mathfrak{T}$ ’s also, then the equations

$$\sum_{\nu} \frac{\partial \mathfrak{T}_{\sigma\nu}}{\partial x_{\nu}} = \frac{1}{2} \sum_{\mu\nu\rho} \frac{\partial g_{\mu\nu}}{\partial x_{\sigma}} \gamma_{\mu\rho} \mathfrak{T}_{\rho\nu} \quad (\sigma = 1, 2, 3, 4) \quad . . . \quad (1)$$

and

$$\sum_{\alpha\beta\mu} \frac{\partial}{\partial x_{\alpha}} \left( \sqrt{-g} \gamma_{\alpha\beta} g_{\sigma\mu} \frac{\partial \gamma_{\mu\nu}}{\partial x_{\beta}} \right) = \kappa (\mathfrak{T}_{\sigma\nu} + t_{\sigma\nu}) \quad (\sigma, \nu = 1, 2, 3, 4) \quad . \quad (2)$$

remain valid, if they were so before the multiplication. But yet it follows by no means from this that a field would be possible, whose  $g$ ’s and  $\mathfrak{T}$ ’s would be the  $\lambda$ -fold of a given field. Rather the contrary may be said to be the case, and this finds its cause in the accessory condition that for infinitely increasing distance to the places where  $\mathfrak{T}_{\sigma\nu}$  differs from zero,  $g_{11}$ ,  $g_{22}$ , and  $g_{33}$  must converge towards  $-1$ ,  $g_{44}$  towards  $c^2$ .

These remarks suffice to make us see that the calculation of fields of gravitation is incomparably more difficult in the new theory than in the old. (NEWTON’s theory). In the latter the field may be found by an integration; in the former theory this is impossible as appears from the above. Now equations (2) are, however, intended to pass

1) I. Entwurf einer verallgemeinerten Relativitätstheorie und einer Theorie der Gravitation, Leipzig bij B. G. TEUBNER. This treatise has been reprinted in ‘Zeitschrift für Mathematik und Physik’, Vol. 62.

II. Kovarianzeigenschaften der Feldgleichungen der auf die verallgemeinerte Relativitätstheorie gegründeten Gravitationstheorie. Zeitschr. für Math. u. Phys., Vol. 63.

into Poisson equations for infinitely weak fields, and so the solution of these equations may be reduced to the solution of Poisson equations, if we content ourselves with successive approximations. We start namely with supposing that the  $g$ 's and  $\gamma$ 's differ little from the values that they must have at infinity; which comes to this that the squares and the products of the differences with those 'values at infinity' are neglected. Then we have to solve ten Poisson equations, and we find the differences multiplied by the factor  $\kappa$ . Then a new correction is introduced, multiplied by the factor  $\kappa^2$ ; this new correction is likewise the solution of a Poisson equation, the second member of which has now, however, been calculated by the aid of the first correction. Going on thus indefinitely, the whole solution is obtained in the form of a power series in  $\kappa$ . For the case of a spherical body, that can be considered as an incompressible fluid, H. A. LORENTZ has calculated the field, neglecting terms which are multiplied by  $\kappa^3$  and higher powers of  $\kappa$ . I have tried to follow the method used in this calculation, as I have understood it from oral communications of Prof. LORENTZ, in calculating the field of two spherical bodies at rest with respect to each other, which I hope to publish in a later communication.

2. The calculation of the field of a single centre requires only that of three functions of the distance to the centre, which may be seen in the following way, given by Prof. LORENTZ.

Let the origin be chosen in the centre of the attracting sphere. It is clear that the  $g$ 's and  $\gamma$ 's can only be functions of the distance  $r$  to the centre. Let  $g_{11} = u$ ,  $g_{22} = g_{33} = v$  and  $g_{44} = w$  in a point  $P$ , lying on the  $x$ -axis. The field being supposed stationary,  $g_{14} = g_{24} = g_{34} = g_{41} = g_{42} = g_{43} = 0$ , and as reversion of one of the three coordinate axes can have no influence on  $ds^2$ , also  $g_{12}$ ,  $g_{13}$ ,  $g_{23}$ ,  $g_{21}$ ,  $g_{31}$  and  $g_{32}$  are zero. Hence

$$\begin{aligned} ds^2 &= u dx^2 + v (dy^2 + dz^2) + w dt^2 \\ &= v (dx^2 + dy^2 + dz^2) + (u-v) dx^2 + w dt^2. \end{aligned}$$

In this expression  $dx^2 + dy^2 + dz^2 = dl^2$  represents the square of an element of length in the space  $(x, y, z)$ ;  $dx^2$  is nothing but  $dr^2$ . We can, therefore, also write

$$ds^2 = v dl^2 + (u-v) dr^2 + w dt^2 \dots \dots \dots (3)$$

and this does not contain anything that refers to the particular situation of the point  $P$ . If we had, therefore, taken  $P$  on an auxiliary axis  $x'$ , i.e. if we had taken  $P$  arbitrary,  $ds^2$  still would have been given by (3). If  $x, y, z$  are the coordinates of  $P$ , then

$$dl^2 = dx^2 + dy^2 + dz^2, \quad dr = \frac{x}{r} dx + \frac{y}{r} dy + \frac{z}{r} dz,$$

hence we get

$$ds^2 = v(dx^2 + dy^2 + dz^2) + (u-v) \left( \frac{x}{r} dx + \frac{y}{r} dy + \frac{z}{r} dz \right)^2 + w dt^2,$$

in which  $u$ ,  $v$ , and  $w$  are functions of  $r$ . From the form of  $ds^2$  we find immediately for the values of the  $g$ 's the scheme

$$\begin{array}{cccc} v + \frac{x^2}{r^2}(u-v) & \frac{xy}{r^2}(u-v) & \frac{xz}{r^2}(u-v) & 0 \\ \frac{xy}{r^2}(u-v) & v + \frac{y^2}{r^2}(u-v) & \frac{yz}{r^2}(u-v) & 0 \\ \frac{xz}{r^2}(u-v) & \frac{yz}{r^2}(u-v) & v + \frac{z^2}{r^2}(u-v) & 0 \\ 0 & 0 & 0 & w \end{array}$$

A similar scheme holds for the  $\gamma$ 's, viz.

$$\begin{array}{cccc} q + \frac{x^2}{r^2}(p-q) & \frac{xy}{r^2}(p-q) & \frac{xz}{r^2}(p-q) & 0 \\ \frac{xy}{r^2}(p-q) & q + \frac{y^2}{r^2}(p-q) & \frac{yz}{r^2}(p-q) & 0 \\ \frac{xz}{r^2}(p-q) & \frac{yz}{r^2}(p-q) & q + \frac{z^2}{r^2}(p-q) & 0 \\ 0 & 0 & 0 & s \end{array}$$

In this  $p$ ,  $q$ , and  $s$  are functions of  $r$  satisfying the relations

$$up = vq = ws = 1, \quad . . . . . (4)$$

which is seen in the simplest way by choosing  $P$  on one of the axes of coordinates.

3. In order to find the differential equations, which  $u$ ,  $v$ , and  $w$  or, what comes to the same thing,  $p$ ,  $q$ , and  $s$  satisfy, we make use of the thesis of the calculus of variations, which occurs in the second paper of EINSTEIN and GROSSMANN cited above, and which states that the first variation of  $\int H d\tau$  is equal to

$$\kappa \int \left( \sum_{\mu\nu} \sqrt{-g} T_{\mu\nu} \delta\gamma_{\mu\nu} \right) d\tau.$$

In this

$$H = \frac{1}{2} \sqrt{-g} \sum_{\alpha\beta\tau\rho} \gamma_{\alpha\beta} \frac{\partial g_{\tau\rho}}{\partial x_\alpha} \frac{\partial \gamma_{\tau\rho}}{\partial x_\beta};$$

the integration is to be performed over a region of the manifold  $(x, y, z, t)$ ,  $d\tau$  is an element of that region, and the variations must

be taken starting from the real (sought) values of the  $g$ 's and the  $\gamma$ 's, and so that they are zero at the boundary of the region.

Let us first calculate  $H$ . We must then differentiate the  $g$ 's and the  $\gamma$ 's with respect to the coordinates; then we can take all the quantities as they are in a point of the  $x$ -axis at a distance  $r = x$  from the origin, and thus we find

$$g_{11} = u, \quad g_{22} = g_{33} = v, \quad g_{44} = w, \quad \gamma_{11} = p, \quad \gamma_{22} = \gamma_{33} = q, \quad \gamma_{44} = s,$$

$$\frac{\partial g_{11}}{\partial x} = u', \quad \frac{\partial g_{22}}{\partial x} = \frac{\partial g_{33}}{\partial x} = v', \quad \frac{\partial g_{44}}{\partial x} = w', \quad \frac{\partial g_{12}}{\partial y} = \frac{\partial g_{21}}{\partial y} = \frac{\partial g_{13}}{\partial z} = \frac{\partial g_{31}}{\partial z} = \frac{u-v}{r},$$

$$\frac{\partial \gamma_{11}}{\partial x} = p', \quad \frac{\partial \gamma_{22}}{\partial x} = \frac{\partial \gamma_{33}}{\partial x} = q', \quad \frac{\partial \gamma_{44}}{\partial x} = s', \quad \frac{\partial \gamma_{12}}{\partial y} = \frac{\partial \gamma_{21}}{\partial y} = \frac{\partial \gamma_{13}}{\partial z} = \frac{\partial \gamma_{31}}{\partial z} = \frac{p-q}{r},$$

$$g = uv^2w.$$

In this the accents denote differentiations with respect to  $r$ ; the values that have not been given are zero.

Let us call  $\sqrt{-g} F$  for brevity. Then on account of (4)

$$F^2 pq^2 s = -1. \quad (5)$$

We find for  $H$

$$H = \frac{1}{2} F \left\{ p(u'p' + 2v'q' + w's') + 4 \frac{q}{r^2} (u-v)(p-q) \right\};$$

as in virtue of (4)

$$q(u-v)(p-q) = q \left( \frac{1}{p} - \frac{1}{q} \right) (p-q) = -p \left( 1 - \frac{q}{p} \right)^2,$$

$$u' = -\frac{p'}{p^2}, \quad v' = -\frac{q'}{q^2} \quad \text{and} \quad w' = -\frac{s'}{s^2},$$

this becomes

$$H = -\frac{1}{2} F p \left\{ \frac{p'^2}{p^2} + 2 \frac{q'^2}{q^2} + \frac{s'^2}{s^2} + \frac{4}{r^2} \left( 1 - \frac{q}{p} \right)^2 \right\}.$$

We now apply the thesis of the calculus of variations to the region

$$t_1 \leq t \leq t_2, \quad r_1 \leq r \leq r_2;$$

then the first variation of  $\int H d\tau$  becomes

$$\delta \int H dt = \delta \int_{t_1}^{t_2} dt \int_{r_1}^{r_2} 4\pi r^2 dr \cdot H = -4\pi (t_2 - t_1) \delta \int_{r_1}^{r_2} L dr,$$

if we put

$$L = -Hr^2 = \frac{1}{2} F p \left\{ \left( \frac{p'^2}{p^2} + 2 \frac{q'^2}{q^2} + \frac{s'^2}{s^2} \right) r^2 + 4 \left( 1 - \frac{q}{p} \right)^2 \right\}. \quad (6)$$

For

$$\alpha \int d\tau \sum_{\mu\nu} \sqrt{-g} T_{\mu\nu} \delta\gamma_{\mu\nu}$$

we find

$$\kappa(t_2 - t_1) \cdot 4\pi \int_{r_1}^{r_2} r^3 dr \cdot F(T_{11}\delta p + T_{22}\delta q + T_{33}\delta q + T_{44}\delta s),$$

so that we get

$$\int_{r_1}^{r_2} d\tau [\delta(-L) - \kappa r^2 F(T_{11}\delta p + T_{22}\delta q + T_{33}\delta q + T_{44}\delta s)] = 0.$$

Now

$$\mathfrak{T}_{\sigma\nu} = \sum_{\mu} \sqrt{-g} \gamma_{\sigma\mu} T_{\mu\nu}$$

and therefore in our case

$$\mathfrak{T}_{\sigma\nu} = \sqrt{-g} \gamma_{\sigma\nu} T_{\sigma\nu},$$

from which follows

$$F T_{11} = \frac{1}{p} \mathfrak{T}_{11}, \quad F T_{22} = \frac{1}{q} F_{22}, \quad F T_{33} = \frac{1}{q} \mathfrak{T}_{33} \quad \text{and} \quad F T_{44} = \frac{1}{s} \mathfrak{T}_{44}.$$

By substituting this and replacing

$$\int_{r_1}^{r_2} \delta(-L) dr \text{ by}$$

$$\int_{r_1}^{r_2} \left[ \left\{ \frac{d}{dr} \left( \frac{\partial L}{\partial p'} \right) - \frac{\partial L}{\partial p} \right\} \delta p + \left\{ \frac{d}{dr} \left( \frac{\partial L}{\partial q'} \right) - \frac{\partial L}{\partial q} \right\} \delta q + \left\{ \frac{d}{dr} \left( \frac{\partial L}{\partial s'} \right) - \frac{\partial L}{\partial s} \right\} \delta s \right] dr,$$

we get, as the coefficients of  $\delta p$ ,  $\delta q$ , and  $\delta s$  must be separately zero,

$$\left. \begin{aligned} \frac{d}{dr} \left( \frac{\partial L}{\partial p'} \right) - \frac{\partial L}{\partial p} &= \kappa \frac{r^2}{p} \mathfrak{T}_{11}, & \frac{d}{dr} \left( \frac{\partial L}{\partial q'} \right) - \frac{\partial L}{\partial q} &= \kappa \frac{r^2}{q} (\mathfrak{T}_{22} + \mathfrak{T}_{33}), \\ \frac{d}{dr} \left( \frac{\partial L}{\partial s'} \right) - \frac{\partial L}{\partial s} &= \kappa \frac{r^2}{s} \mathfrak{T}_{44}. \end{aligned} \right\} \quad (7)$$

In this  $F$  must be looked upon as a known function of  $p$ ,  $q$ , and  $s$ , given by (5).

The tensor  $\mathfrak{T}_{\sigma\nu} : \sqrt{-g}$  possesses the same symmetry properties as  $g_{\sigma\nu}$ . Of the equations (1) only the first does not pass into an identity, but into

$$\frac{dP}{dr} + \frac{2}{r} (P - Q) + \frac{1}{2} \left( \frac{p'}{p} P + 2 \frac{q'}{q} Q + \frac{s'}{s} S \right) = 0, \dots \quad (8)$$

if we put  $\mathfrak{T}_{11} = P$ ,  $\mathfrak{T}_{22} = \mathfrak{T}_{33} = Q$  and  $\mathfrak{T}_{44} = S$ .

Then this equation with the three equations (7) form a system of four differential equations for the determination of  $p$ ,  $q$ , and  $s$ , and say  $P$ , if, in connection with the nature of the substance, we know two more relations between  $P$ ,  $Q$ , and  $S$ . If e.g.  $Q = P$  and  $S = const.$ , we have the case of an incompressible fluid;  $Q = P$ ,  $S = f(P)$  represents the case of a compressible liquid or gas.

4. In some cases it is possible to derive another relation from (7) and (8), in which only first derivatives occur, a so-called first integral. For this purpose we multiply the equations (7) successively by  $p'$ ,  $q'$ , and  $s'$ , and we then add them. The result may be written in the form

$$\frac{d}{dr} \left[ p' \frac{\partial L}{\partial p'} + q' \frac{\partial L}{\partial q'} + s' \frac{\partial L}{\partial s'} \right] + \frac{\partial L}{\partial r} - \frac{dL}{dr} = \kappa r^2 \left( \frac{p'}{p} P + 2 \frac{q'}{q} Q + \frac{s'}{s} S \right).$$

From (6) we find that

$$p' \frac{\partial L}{\partial p'} + q' \frac{\partial L}{\partial q'} + s' \frac{\partial L}{\partial s'} - L = \frac{1}{2} \epsilon p \left\{ \left( \frac{p'^2}{p^2} + 2 \frac{q'^2}{q^2} + \frac{s'^2}{s^2} \right) r^2 - 4 \left( 1 - \frac{q}{p} \right)^2 \right\}$$

and

$$\frac{\partial L}{\partial r} = \epsilon p r \left( \frac{p'^2}{p^2} + 2 \frac{q'^2}{q^2} + \frac{s'^2}{s^2} \right)$$

so that we get in connection with (8)

$$\left. \begin{aligned} & \frac{d}{dr} \left[ \frac{1}{2} \epsilon p \left\{ \left( \frac{p'^2}{p^2} + 2 \frac{q'^2}{q^2} + \frac{s'^2}{s^2} \right) r^2 - 4 \left( 1 - \frac{q}{p} \right)^2 \right\} \right] + \\ & + \epsilon p r \left( \frac{p'^2}{p^2} + 2 \frac{q'^2}{q^2} + \frac{s'^2}{s^2} \right) = - 2 \kappa r^2 \frac{dP}{dr} - 4 \kappa r (P - Q) \end{aligned} \right\} \quad (9)$$

For the equations (7), written in full, we find, after having multiplied them successively by  $p$ ,  $\frac{1}{2}q$ , and  $s$ ,

$$\left. \begin{aligned} & \frac{d}{dr} \left( r^2 \epsilon p \frac{p'}{p} \right) - \frac{1}{2} L - 4 \epsilon p \left( 1 - \frac{q}{p} \right) \frac{q}{p} = \kappa r^2 P \\ & \frac{d}{dr} \left( r^2 \epsilon p \frac{q'}{q} \right) - \frac{1}{2} L + 2 \epsilon p \left( 1 - \frac{q}{p} \right) \frac{q}{p} = \kappa r^2 Q \\ & \frac{d}{dr} \left( r^2 \epsilon p \frac{s'}{s} \right) + \frac{1}{2} L = \kappa r^2 S. \end{aligned} \right\} \quad (10)$$

We now add twice the second equation to the first, and get in this way

$$\frac{d}{dr} \left[ r^3 \epsilon p \left( \frac{p'}{p} + 2 \frac{q'}{q} \right) \right] + \frac{1}{2} L = \kappa r^2 (P + 2Q). \quad (11)$$

When we subtract twice (11) from  $r$  times (9) we find

$$\begin{aligned} & r \frac{d}{dr} \left[ \frac{1}{2} \epsilon p \left\{ \left( \frac{p'^2}{p^2} + 2 \frac{q'^2}{q^2} + \frac{s'^2}{s^2} \right) r^2 - 4 \left( 1 - \frac{q}{p} \right)^2 \right\} \right] - \\ & - 2 \frac{d}{dr} \left[ r^3 \epsilon p \left( \frac{p'}{p} + 2 \frac{q'}{q} \right) \right] + \frac{1}{2} \epsilon p \left\{ \left( \frac{p'^2}{p^2} + 2 \frac{q'^2}{q^2} + \frac{s'^2}{s^2} \right) r^2 - 4 \left( 1 - \frac{q}{p} \right)^2 \right\} = \\ & = - 2 \kappa \left\{ r^3 \frac{dP}{dr} + r^2 (2P + Q) \right\} \end{aligned}$$

or

$$\frac{d}{dr} \left[ \frac{1}{2} \epsilon p r \left\{ \left( \frac{p'^2}{p^2} + 2 \frac{q'^2}{q^2} + \frac{s'^2}{s^2} \right) r^2 - 4 \left( 1 - \frac{q}{p} \right)^2 \right\} - 2 \epsilon p r^3 \left( \frac{p'}{p} + 2 \frac{q'}{q} \right) \right] =$$

$$= - 2\kappa \left\{ r^3 \frac{dP}{dr} + r^2 (2P + Q) \right\}.$$

For a fluid  $Q = P$ , and

$$\frac{1}{2} \epsilon p r \left\{ \left( \frac{p'^2}{p^2} + 2 \frac{q'^2}{q^2} + \frac{s'^2}{s^2} \right) r^2 - 4 \left( 1 - \frac{q}{p} \right)^2 \right\} - 2 \epsilon p r^3 \left( \frac{p'}{p} + 2 \frac{q'}{q} \right) + \left. \right\} (12)$$

$$+ 2\kappa r^3 P = const.$$

In this case therefore we have a first integral. If  $S$  is only different from zero, when  $r \leq R$ , the same thing is the case with  $P$  and  $Q$ , whether  $P$  be equal to  $Q$  or not. For  $r > R$  (12) then becomes always a first integral, if we put  $P = 0$ . In this case we can get another first integral for  $r > R$ , by subtracting the third equation (10) from (11), viz.:

$$r^2 \epsilon p \left( \frac{p'}{p} + 2 \frac{q'}{q} - \frac{s'}{s} \right) = const. \dots \dots (13)$$

5. I have not succeeded in finding other first integrals of the system (10); in what follows we shall therefore content ourselves with the calculation of the approximation already found by LORENTZ; but we shall for this purpose start from the equations (10), and besides we shall not suppose  $\mathfrak{T}_{44}$  to be constant. However intricate the way may be in which the different quantities  $\mathfrak{T}_{\alpha\beta}$  depend on each other and on the field,  $\mathfrak{T}_{44}$  can only depend on  $r$ ; hence we put

$$\mathfrak{T}_{44} = \varrho(r).$$

We suppose the values of the other  $\mathfrak{T}$ 's only different from zero in consequence of the gravitation and therefore we may suppose these values to be zero in first approximation. We now think  $p, q$ , and  $s$  expanded in a series of powers of  $\kappa$ , and the expansion broken off after the term of the first degree in  $\kappa$ . We then find from (10), neglecting terms with  $\kappa^2$  etc.,

$$\frac{d}{dr} (r^2 p') = 4 (p - q), \quad \frac{d}{dr} (r^2 q') = - 2 (p - q), \quad \frac{d}{dr} (r^2 s') = - \frac{\kappa Q}{c^3} r^2.$$

From the first two equations it follows, that

$$r^2 (p' + 2q') = const. \quad \text{and} \quad r^2 (p' - q') = const.$$

As  $p'$  and  $q'$  must be infinite for  $r = 0$ , the two constants appear to be zero, hence  $p' = q' = 0$  and  $p = q = - 1$ . No terms of the first order will occur, therefore, in  $p$  and  $q$ . Further

$$r^2 s' = -\frac{\kappa}{c^3} \int_0^r Q r^2 dr = -\frac{\kappa}{c^3} a(r),$$

if we put

$$\int_0^r Q r^2 dr = a(r).$$

Hence

$$s = \frac{1}{c^2} + \frac{\kappa}{c^3} \int_r^\infty \frac{a}{r^2} dr.$$

Let this approximation of  $s$  be called  $s_1$ . We now go a step further, by retaining the terms with  $\kappa^2$  in  $p, q, s$ , and in the equations (10). We may put

$$L = -\frac{1}{2} c^5 r^2 s_1'^2 = -\frac{1}{2} \frac{\kappa^2 a^2}{c r^2}.$$

We now put

$$s = s_1 + \zeta,$$

which makes the third equation (10) pass into

$$-\frac{d}{dr} \left[ r^2 F \frac{s_1'}{s_1} + c^3 r^2 \zeta' \right] - \frac{\kappa^2 a^2}{4 c r^2} = \kappa r^2 Q.$$

Now, up to the terms of the first order,

$$\frac{F}{s_1} = s_1^{-\frac{3}{2}} = c^3 \left( 1 + \frac{\kappa}{c} \int_r^\infty \frac{a}{r^2} dr \right)^{-\frac{3}{2}} = c^3 \left( 1 - \frac{3\kappa}{2c} \int_r^\infty \frac{a}{r^2} dr \right),$$

so that we find

$$-\frac{d}{dr} (c^3 r^2 \zeta') - \frac{d}{dr} (r^2 c^3 s_1') + \frac{3\kappa}{2c} \frac{d}{dr} \left( r^2 c^3 s_1' \int_r^\infty \frac{a}{r^2} dr \right) - \frac{\kappa^2 a^2}{4 c r^2} = \kappa r^2 Q,$$

which in consequence of

$$\frac{d}{dr} (r^2 s_1') = -\frac{\kappa Q}{c^3} r^2$$

passes into

$$\frac{d}{dr} (r^2 \zeta') = -\frac{3\kappa^2}{2c^4} \frac{d}{dr} \left( a \int_r^\infty \frac{a}{r^2} dr \right) - \frac{\kappa^2 a^2}{4c^4 r^2}.$$

From this we find

$$\zeta = \frac{3\kappa^2}{2c^4} \int_r^\infty \frac{a}{r^2} dr \int_r^\infty \frac{a}{r^2} dr + \frac{\kappa^2}{4c^4} \int_r^\infty \frac{dr}{r^2} \int_0^r \frac{a^2}{r^2} dr$$

and therefore

$$s = \frac{1}{c^2} + \frac{\kappa}{c^3} \int_r^\infty \frac{a}{r^2} dr + \frac{\kappa^2}{c^4} \left\{ \frac{3}{2} \int_r^\infty \frac{a}{r^2} dr \int_r^\infty \frac{a}{r^2} dr + \frac{1}{4} \int_r^\infty \frac{dr}{r^2} \int_0^r \frac{a^2}{r^2} dr \right\}.$$

At a great distance from the attracting centre we may put  $a = a_\infty$  (constant) and  $\rho = 0$ . In this way we get

$$s = \frac{1}{c^2} + \frac{\kappa a_\infty}{c^3 r} + \frac{\kappa^2}{4c^4 r} \int_0^\infty \frac{a^2}{r^2} dr + \frac{5\kappa^2 a_\infty^2}{8c^4 r^2}.$$

If we now put

$$\frac{1}{2} \kappa a_\infty + \frac{1}{4} \kappa^2 \int_0^\infty \frac{a^2}{r^2} dr = k,$$

we may write  $4k^2/c^2 a_\infty^2$  for  $\kappa^2$  in the last term of  $s$ , and so we find

$$s = \frac{1}{c^2} \left( 1 + \frac{2k}{c^2 r} + \frac{5k^2}{2c^4 r^2} \right) \dots \dots \dots (14)$$

We further put

$$p = -1 + \xi, q = -1 + \eta.$$

The first and second of the equations (10) then become

$$\begin{aligned} \frac{d}{dr} (r^2 \xi') - 4 (\xi - \eta) + \frac{\kappa^2 a^2}{4c^2 r^2} &= \frac{\kappa}{c} P r^2, \\ \frac{d}{dr} (r^2 \eta') + 2 (\xi - \eta) - \frac{\kappa^2 a^2}{4c^2 r^2} &= \frac{\kappa}{c} Q r^2, \end{aligned}$$

from which it follows that

$$\left. \begin{aligned} \frac{d}{dr} [r^2 (\xi' + 2\eta')] &= \frac{\kappa}{c} r^2 (P + 2Q) + \frac{\kappa^2 a^2}{4c^2 r^2}, \\ \frac{d}{dr} [r^2 (\xi' - \eta')] - 6 (\xi - \eta) &= \frac{\kappa}{c} r^2 (P - Q) - \frac{\kappa^2 a^2}{2c^2 r^2}. \end{aligned} \right\} \dots \dots (15)$$

In this  $P$  and  $Q$  must be calculated up to the terms of the first order, which can take place by the aid of an equation, that follows from (8) viz.

$$\frac{dP}{dr} + \frac{2}{r} (P - Q) = \frac{\kappa \rho a}{2c r^2},$$

if one more relation is given between  $P$  and  $Q$ . If e.g.  $P = Q$ , then

$$\xi + 2\eta = \frac{\kappa^2 a^3}{8c^2 r^2} + \frac{\kappa^2}{2c^2} \int_r^\infty a \rho dr - \frac{\kappa^2 r^2}{4c^2} \int_r^\infty \frac{a \rho}{r^2} dr,$$

$$\xi - \eta = \frac{\kappa^2 r^2}{10e^2} \int_r^\infty \frac{\alpha^2}{r^5} dr + \frac{\kappa^2}{10e^2 r^3} \int_0^r \alpha^2 dr.$$

But whatever may be the particular properties of the central body, we can put  $P = Q = \varrho = 0$  and  $\alpha = \alpha_\infty$  at a large distance, in consequence of which we find from (15)

$$\xi + 2\eta = \frac{\kappa^2 \alpha_\infty^2}{8e^2 r^2}, \quad \xi - \eta = \frac{\kappa^2 \alpha_\infty^2}{8e^2 r^2} + \frac{3B}{r^3},$$

in which  $B$  is a constant of the second order.

From this it follows that

$$p = -1 + \frac{\kappa^2 \alpha_\infty^2}{8e^2 r^2} + \frac{2B}{r^3}, \quad q = -1 - \frac{B}{r^3}.$$

6. We shall now examine how a particle moves in the field of a single centre.

The motion is determined by a principle corresponding to that of HAMILTON, viz.

$$\delta \int_{t_1}^{t_2} L dt = \delta \int_{t_1}^{t_2} dt \sqrt{g_{11} \dot{x}_1^2 + \dots + g_{44}} = 0.$$

In the case under consideration, we have

$$ds^2 = v(dx^2 + dy^2 + dz^2) + (u-v) dr^2 + w dt^2.$$

If we introduce polar coordinates  $r, \vartheta, \varphi$ , we get

$$ds^2 = w dt^2 + u dr^2 + vr^2 d\vartheta^2 + vr^2 \sin^2 \vartheta d\varphi^2,$$

hence

$$L = \sqrt{w + ur^2 + vr^2 \dot{\vartheta}^2 + vr^2 \sin^2 \vartheta \dot{\varphi}^2}.$$

One of the three equations of motion is

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\vartheta}} \right) = 0.$$

which shows that if  $\dot{\vartheta}$  once is zero, it remains so; we see from this that the motion takes place in a plane, and, knowing this, we can choose the coordinates so that this plane becomes the plane  $\vartheta = \frac{\pi}{2}$ .

Accordingly

$$L = \sqrt{w + ur^2 + vr^2 \dot{\varphi}^2}$$

and the equations of motion become:

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{r}} \right) = \frac{\partial L}{\partial r} \quad \text{and} \quad \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\varphi}} \right) = 0. \quad \dots \quad (16)$$

The equation of energy

$$L - \dot{r} \frac{\partial L}{\partial \dot{r}} - \dot{\varphi} \frac{\partial L}{\partial \dot{\varphi}} = \text{constant}$$

and the equation

$$\frac{\partial L}{\partial \dot{\varphi}} = \text{constant}$$

are first integrals, which together can replace the equations of motion. If we call the first constant  $h$  and the second  $Ah$ , then

$$\frac{w}{\sqrt{w + ur^2 + vr^2 \dot{\varphi}^2}} = h \quad . \quad . \quad . \quad (17)$$

and

$$\frac{-v}{w} r^2 \dot{\varphi} = A. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

By these two equations  $\varphi$  and  $r$  are given as functions of  $t$ ; (18) presents close resemblance to KEPLER'S second law.

Eliminating  $\dot{\varphi}$  from (17) and (18), we find

$$u \left( \frac{dr}{dt} \right)^2 = w^2 \left( \frac{1}{h^2} - \frac{A^2}{vr^2} \right) - w,$$

by which  $r$  is defined as a function of  $t$ ; (18) then gives  $\varphi$  as a function of  $t$ .

In the case that the orbit just extends into infinity,  $\dot{r}^2 + r^2 \dot{\varphi}^2$ , and also  $ur^2 + vr^2 \dot{\varphi}^2$  must be zero for  $r = \infty$ , hence  $h = c$  according to (17). If  $h < c$ , then  $r$  remains finite, and if  $h > c$ , the velocity is different from zero also for infinitely increasing  $r$ .

The orbit may also be circular; as in virtue of (18)  $\dot{\varphi}$  is constant in this case,  $\partial L / \partial \dot{r}$  will be constant, and the first equation (16) shows that

$$\frac{\partial L}{\partial r} = 0,$$

i. e.

$$\frac{dw}{dr} + \dot{\varphi}^2 \frac{d}{dr} (vr^2) = 0,$$

by which the angular velocity is determined as a function of  $r$ .

7. In order to examine closer the motion of a particle we make use of the approximations for  $u$ ,  $v$ , and  $w$ , found above. If we put in (17)

$$u = v = -1, \quad w = c^2 \left( 1 - \frac{2k}{c^2 r} \right),$$

we get, expanding the root,

$$\frac{k}{c^2 r} - \frac{\dot{r}^2 + r^2 \dot{\varphi}^2}{2c^2} = 1 - \frac{h}{c}; \quad \dots \dots \dots (17a)$$

and from (18) we find, by putting  $v = -1$  and  $w = c^2$ ,

$$r^2 \dot{\varphi} = A c^2 \quad \dots \dots \dots (18a)$$

The formulae (17a) and (18a) lead to the ordinary planetary motion as described by KEPLER'S laws. We now shall go a step further with the approximation. Equation (17a) shows that  $k/cr^2$  and  $\dot{r}^2 + r^2 \dot{\varphi}^2/c^2$  are of the same order of magnitude; both quantities are small, as the second represents the square of the ratio of the planetary velocity to the velocity of light. We shall call these quantities (also  $1-h/c$ ) of the first order of magnitude, and we wish to retain in (17) also the quantities of the second order of magnitude. For this purpose we still need not go further in  $u$  and  $v$  than to terms without  $\alpha$ , as  $\xi$  and  $\eta$  contain the factor  $\alpha^2$ , and are of the second order of magnitude, but would give terms of the third order of magnitude in (17), because they occur there multiplied by  $\dot{r}^2$  and  $r^2 \dot{\varphi}^2$ . The motion of the material point will, accordingly, not depend on the special properties of the substance of the attracting body.

Let us now put for brevity

$$1 - \frac{h}{c} = l, \quad w = c^2(1 - \sigma + \varepsilon),$$

in which  $l$  and  $\sigma$  are of the first order,  $\varepsilon$  of the second order in  $\alpha$ . We now expand the root in (17), and omit terms of higher order than the second; this implies that in the terms of the second order we may apply equation (17a), i.e.:

$$\frac{\dot{r}^2 + r^2 \dot{\varphi}^2}{2c^2} = \frac{1}{2}\sigma - l,$$

in order to eliminate  $\dot{r}^2 + r^2 \dot{\varphi}^2$  from the terms of the second order. The result is

$$\dot{r}^2 + r^2 \dot{\varphi}^2 = -2c^2 l(1 + \frac{3}{2}l) + c^2 \sigma(1 + 4l) - c^2(\varepsilon + \sigma^2). \quad \dots (17b)$$

To proceed a step further with the approximation in (18), we need only put  $v = -1$  and  $w = c^2(1 - \sigma)$ ; this gives

$$r^2 \dot{\varphi} = A c^2(1 - \sigma). \quad \dots \dots \dots (18b)$$

In connection with this we may write for (17b)

$$\frac{1}{r^4} \left( \frac{dr}{d\varphi} \right)^2 + \frac{1}{r^2} = -\frac{2l}{A^2 c^2} \left( 1 + \frac{3}{2}l \right) + \frac{\sigma}{A^2 c^2} + \frac{\sigma^2 - \varepsilon}{A^2 c^2}.$$

As  $ws = 1$  we get

$$s = \frac{1}{c^2} \{ 1 + \sigma + (\sigma^2 - \varepsilon) \}.$$

If we compare this with (14), and moreover put  $r\xi = 1$ , then

$$\left(\frac{d\xi}{d\varphi}\right)^2 + \xi^2 = -\frac{2l}{A^2c^2} \left(1 + \frac{3}{2}l\right) + \frac{2k}{A^2c^4} \xi + \frac{5k^2}{2A^2c^6} \xi^2.$$

The function

$$\xi = \alpha + \beta \cos \gamma(\varphi + C)$$

solves this differential equation by suitable choice of the values  $\alpha$ ,  $\beta$ , and  $\gamma$ ; we can take the integration constant  $C$  to be zero, as this choice only determines from where we measure  $\varphi$ . The function

$$\xi = \alpha + \beta \cos \gamma\varphi$$

satisfies the differential equation, if

$$\frac{2}{A^2c^2} l(1 + \frac{3}{2}l) = (\alpha^2 - \beta^2)\gamma^2, \quad \frac{k}{A^2c^4} = \alpha\gamma^2, \quad 1 - \frac{5k^2}{2A^2c^6} = \gamma^2.$$

Instead of the integration constants  $l$  and  $A$ , which we introduced before, we can now consider  $\alpha$  and  $\beta$  as such.  $\gamma$  differs from 1 only in terms of the second order, and therefore the equation

$$\alpha = \frac{k}{A^2c^4}$$

is accurate up to terms of the second order.

We may, therefore, use the value of  $A^2c^4$ , which follows from this, for the calculation of  $\gamma$ , and so we find

$$\gamma^2 = 1 - \frac{5k}{2c^2} \alpha,$$

and from this

$$\frac{1}{\gamma} - 1 = \frac{5k}{4c^2} \alpha.$$

If we now put  $\gamma\varphi = \psi$ , then

$$\varphi = \psi + \frac{5k}{4c^2} \alpha\psi$$

and

$$\xi = \frac{1}{\gamma} = \alpha + \beta \cos \psi \dots \dots \dots (19)$$

This is the equation of a conic section in polar coordinates.

The angle  $\frac{5ka\psi}{4c^2}$ , between the major axis and the fixed line  $\varphi = 0$ , is proportional to the angle  $\psi$ , between the radius vector and the major axis. For one revolution the 'motion of the perihelium' is  $450 ka/c^2$  degrees; it depends only on the parameter  $1/a$  of the orbit. As Prof. DE SITTER has calculated from equations of motion determined by Prof. LORENTZ, it amounts for Mercurius to  $18''$  per century, the observed motion being  $44''$ . It is worthy of note that the motion of the perihelium does not depend

on the particular properties of the substance of which the centre of attraction consists.

The time of revolution  $T$  (the time in which  $\varphi$  increases by  $2\pi$ ) can easily be calculated. It follows namely from (18<sup>b</sup>) and (19) that

$$\dot{\psi} = Ac^2\gamma(a + \beta \cos \psi)^2 \left\{ 1 - \frac{2k}{c^2} (a + \beta \cos \psi) \right\},$$

and from this, accurate up to quantities of the second order of magnitude,

$$Ac^2\gamma dt = \frac{d\psi}{(a + \beta \cos \psi)^2} + \frac{2k}{c^2} \frac{d\psi}{a + \beta \cos \psi}.$$

From this it easily follows, that

$$Ac^2T = \frac{2\pi}{\sqrt{\alpha^2 - \beta^2}} \left( \frac{\alpha}{\alpha^2 - \beta^2} + \frac{k}{c^2} \right).$$

Let us call  $a$  half the major axis of the ellipse, then

$$a = \frac{\alpha}{\alpha^2 - \beta^2}$$

and we get

$$a \left( a + \frac{k}{c^2} \right)^2 : T^2 = \frac{k}{4\pi^2}.$$

$T$  depends therefore still exclusively on the major axis of the orbit; this is, however, not the case with the time of revolution in the ellipse. In the first member we may substitute  $4\pi^2 a^3 / c^2 T^2$  for  $k/c^2$ , and thus we get

$$a^3 \left[ 1 + \frac{2}{3} \left( \frac{2\pi a}{cT} \right)^2 \right]^3 : T^2 = \frac{k}{4\pi^2}$$

instead of the third law of KEPLER.

**Chemistry.** — “On gas equilibria, and a test of Prof. J. D. VAN DER WAALS Jr.’s formula”. II. By Dr. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of Dec. 30, 1914.)

### 7. The equilibrium $I_2 \rightleftharpoons 2I$ . (Continued).

In my preceding paper<sup>1)</sup> I have shown that from the determinations of the iodine equilibrium the value  $0.41 \cdot 10^{-8}$  cm. follows for the radius of inertia of the iodine molecule; the iodine dissociation can therefore be represented by equation 8, when  $\lambda = 15\mu$  and  $\log M = -38.20$  are there substituted. That this equation sufficiently represents the experimentally found values, appears from

<sup>1)</sup> These Proc. 17, 695 (1914/15).

table V, in which the value 34690 cal. has been chosen for  $\sum n E_{T=0}$  so that in my opinion the most probable expression for the dissociation constant is as follows:

$$\log K = -\frac{7589}{T} + \frac{1}{2} \log T + \log \left( 1 - e^{-\frac{972}{T}} \right) + 1.887 \quad (13)$$

TABLE V.

<i>t</i> (Cels)	<i>T</i>	<i>log K</i> (found)	<i>log K</i> (calc.)	difference
800	1073	0.111-4	0.104-4	- 0.007
900	1173	0.692-4	0.703-4	+ 0.011
1000	1273	0.199-3	0.206-3	+ 0.007
1100	1373	0.639-3	0.634-3	- 0.005
1200	1473	0.009-2	0.003-2	- 0.006

The discrepancies between the found and the calculated values are smaller than the errors of observation.

8. Before proceeding with the calculation of chemical equilibria by the aid of the expressions for the gas entropy mentioned in § 2 and Prof. VAN DER WAALS Jr.'s expression mentioned in § 4, I will discuss the results at which STERN has arrived in his paper, which I mentioned in the "Postscript" of my latest communication.

The expressions for the gas entropy used by STERN, deviate in a very essential point from those mentioned in § 2. The entropy of a gas is determined by STERN with respect to the solid state at  $T = 0$  as zero condition. The expression for monatomic gases agrees with equation 1 of my first paper, when there the value

$$\frac{3}{2} R \ln 2\pi + \frac{5}{2} R + S_{\text{solid at } T=0}$$

is substituted for  $C_1$ . In the same way the value of a di-atomic gas is indicated by equation 2, if  $\frac{7}{2} R + S_{\text{solid at } T=0}$  is taken for  $C_2$ . It is clear that in contrast with the application of the entropy values of § 2, therefore according to STERN the algebraic sum of the entropies of the solid substances at  $T = 0$  occurs in the expressions

1) Besides STERN takes the vibration in the diatomic molecule into account, which in equation 2 necessitates the addition of an expression with  $\nu$ . Also the variability of the specific heats is therefore taken into account with this expression.

for the equilibrium constant of the gas equilibrium. Hence whereas the expressions of § 2, which were exclusively derived from gas properties, leave the value for the entropy of solid out of account, and the calculations of the gas equilibria have nothing to do with the solid state either, so that the determination of the entropy of solid according to  $S = k \log W$  remains a separate problem, the test of STERN's expressions can give a decision of the validity of NERNST's theorem of heat. If we assume STERN's derivations for the gas entropy to be correct, then on application to the iodine equilibrium it appears that the algebraic sum of the entropies of the solid substances at  $T=0$  is not zero, which it ought to be according to the heat theorem, but about  $-7$ . In this test it is assumed that the moment of inertia of the iodine molecules has the value that would follow from the mean molecule radius for iodine (from the index of refraction). We have here, however, two quantities at our disposal: the moment of inertia and  $\Sigma S_{solid}$ . It is clear that reversely the assumption that the sum of the entropies of the solid substances at  $T=0$  is zero (through which this algebraic sum disappears from the constant of equilibrium and the expression deviates from that of Prof. VAN DER WAALS JR. only in this that it is assumed in the former that the specific heat of the vibration has already reached its amount of equipartition) changes the value of the moment of inertia. On this assumption it gets about the value which was indicated in my first paper.

9. The objection advanced by STERN against a small moment of inertia, is founded on the value of the chemical constant of  $I_2$ , which was calculated by SACKUR on the assumption of the mean molecule radius (from the index of refraction) for the moment of inertia, and with which the vapour pressure values of solid iodine can very well be represented as appears from SACKUR's test.<sup>1)</sup> In virtue of this, however, I do not think myself justified in rejecting the moment of inertia calculated by me.

The said test of the vapour pressure line has been carried out by SACKUR on simultaneous assumption of the expression 2 of § 2 and of  $S_{solid} \text{ at } T=0 = 0$ . We are then led to the question whether these two assumptions are identical or in conflict with each other. Discussions with Prof. VAN DER WAALS JR. concerning this question have led us to the following opinion. If the entropy of a gas is determined by means of  $k \log W$ , the expressions 1 and 2 of § 2 are found for

<sup>1)</sup> SACKUR, Ann. der Physik (4) 40 87 (1913).

it; these values are entirely independent of the entropy of the solid substance. The gas entropy is namely found then by examining the probability of the gas state; if this is done at temperatures where solid substance is impossible, so far above the melting-point, the chance to a solid configuration must be entirely excluded. When the iodine equilibrium is tested, where the temperatures amount to  $1000^{\circ}$  K. and more, the chance to solid substance (melting point  $387^{\circ}$  K.) may certainly be put zero. And therefore the expressions of SACKUR, TETRODE, and VAN DER WAALS will in my opinion yield the correct values for the moment of inertia, and the test remains entirely outside the theorem of heat, in whatever form it be.

If, however, for the entropy of gas  $k \log W$  has been chosen — I will call these values the gas scale for the entropy — it is the question what will be the entropy of solid. This value might either be determined by means of  $dS = \frac{dQ}{T}$ , or by applying the expression  $k \log W$  also to the solid state. The latter, however, is only feasible on the assumption of one or more hypotheses concerning the constitution of the solid substance; these derivations must, therefore, certainly remain arbitrary in a high degree. For a mono-atomic solid substance a comparatively simple mechanism may be devised corresponding to the properties of solid <sup>1)</sup>, but for multi-atomic solid substances the model becomes necessarily more intricate, hence more arbitrary. <sup>2)</sup>

If it is, however, assumed, as is often done, that the entropy of solid at  $T = 0$  is zero, then starting from this the entropy of other states can be determined with the aid of  $dS = \frac{dQ}{T}$ . This scale of entropy, which I will call the scale for solid, need not coincide, however, with the gas scale in my opinion. And if it does so for one substance, this need not necessarily be the case for all. At any rate this coinciding of the two scales requires experimental verification.

The only data from the literature which can furnish such a test, are in my opinion:

1. the theoretical derivations of STERN's gas entropy.
2. the vapour pressure line of mercury.
3. the calculation of  $\sum_{\text{solid } T=0}^{\text{gas}} \frac{dQ}{T}$  for iodine.

<sup>1)</sup> STERN, Physik. Zeitschr. **14** 629 (1913).

<sup>2)</sup> STERN, Ann. der Physik. (4) **44** 520 (1914).

1. STERN's derivations rest on the above mentioned assumptions concerning the mechanism of solid substance. STERN's expressions and those of § 2 agree in a high degree, but that in his expressions the constant part has been accurately represented holds only for the definite conception which STERN forms for the solid substance<sup>1)</sup>. A rigorous proof for the coincidence of the two scales is in my opinion not furnished by this derivation.

2. The testing of the mercury line seems to plead for the coincidence of the two scales. In a recent paper in these Proceedings Prof. LORENTZ carries out a similar test<sup>2)</sup>. In connection with the above I think I can state the result as follows: If coincidence of the above mentioned scales is assumed, the dimension of the "elementary regions" appears to be about  $h^3$ , but as the coincidence of the scales is not proved, little weight is to be attached to the conclusion concerning the extent of the "elementary regions". This is probably a too rigorous statement of the conclusion of the mentioned paper; for the other difficulties which attend this testing, I must refer to the cited paper. Let us now consider that the entropies of § 2 (of my preceding paper) rest on the assumption that the area of the regions is really  $h^3$ ; then at least if the expressions are correct and may therefore be applied to the evaporation, the coincidence of the two scales would become probable for this case.

3. From the caloric data on iodine STERN has calculated the difference of entropy between solid iodine ( $I_2$ ) at  $T=0$  and gaseous iodine (in atomic state) at  $T=323$ <sup>3)</sup>. STERN now uses for the entropy of the gaseous atomic iodine the expression which was derived by him for monatomic gases, and in which (see § 8) the entropy of solid atomic iodine at  $T=0$  is taken as zero. It is clear that in this way the algebraic sum of the entropies of the solid substances at  $T=0$  can be calculated.

If, however, the values of § 2 are introduced for the entropy of atomic gaseous iodine, we do not find in this way the algebraic sum of the entropies of the solid substances, but only the entropy of solid iodine ( $I_2$ ) at  $T=0$ . If, therefore, the entropies of § 2 are assumed as the correct ones, it follows from this calculation that the entropy of solid iodine ( $I_2$ ) at  $T=0$  does not become zero, but  $-7.6$ . Thus interpreted, this would plead against the coinciding of the two entropy scales for iodine.

10. With this interpretation I think I can also get agreement with

<sup>1)</sup> STERN, l. c.

<sup>2)</sup> Verslagen Kon. Ak. Amsterdam, 23. 515. (1914/15), (still to be translated).

<sup>3)</sup> STERN, Ann. der Physik. (4) 44 513 et seq. (1914).

the determinations of the vapour tension of solid iodine. The "chemical constant" of iodine, which is given by  $C = \frac{S'_{gas} - c_p + R \ln R - S_{solid T=0}}{2.3 R}$ ,

in which  $S'_{gas}$  represents the entropy constant according to the gas scale, and in which  $S_{solid T=0}$  is generally also put zero (which in my opinion need not therefore be the case in the gas scale), is 3,27 according to SACKUR<sup>1</sup>). The entropy constant of the gas is calculated by SACKUR on the assumption that the moment of inertia calculated from the mean molecule radius (index of refraction) is the correct one. As the radius of inertia calculated by me in my first paper, is  $\frac{2.26}{0.41}$  or 5.5 times smaller, and the moment of inertia therefore about 30 times smaller, the value of  $S'_{gas}$ , in which the moment of inertia  $M$  occurs as  $R \ln M^2$ , would become  $R \ln 30$  or 6,75 times smaller when the value found by me is used. Hence if we want to retain the value 3,27 for the "chemical constant",  $S_{solid T=0}$  must not be taken zero, but  $-6,75$ , which is in satisfactory agreement with the result at the end of § 9. I think therefore I am justified in taking this as a confirmation of the validity of my former calculation.

11. I would therefore summarize the above as follows:

1. from the vapour pressure line of mercury the entropy of solid mercury appears to be about zero at the absolute zero point in the gas scale.

2. it follows from the caloric data of iodine that the entropy of solid iodine ( $I_2$ ) at  $T=0$  is about  $-7$ .

3. it appears from the calculation of my preceding communication that the radius of inertia of  $I_2$  is about five times smaller than the mean molecule radius determined from the index of refraction.

4. when this radius of inertia is used the test of the vapour pressure line of iodine yields for the entropy of solid iodine a value of about  $-7$  in agreement with the second conclusion.

5. the cited data do not allow of a test of the theorem of heat.

6. In agreement with the third conclusion MANDERSLOOT'S calculations lead to moments of inertia which are smaller than would agree with the mean molecule radii (index of refraction, internal friction, and  $b$ -values of the equation of state<sup>3</sup>).

<sup>1</sup>) SACKUR, l. c.

<sup>2</sup>) These Proceedings, Vol. XVII p. 697, (equation 2).

<sup>3</sup>) MANDERSLOOT, Thesis for the Doctorate. Utrecht, 1914. See also: These Proc. Vol. XVII, p. 702. (1914/15).

12. *Other equilibria of the type  $AB \rightleftharpoons A + B$ .*

None of the data which are to be found in the literature on other equilibria of the above type, allow of a sufficiently accurate calculation of the moments of inertia.

There exists a very interesting investigation on hydrogen dissociation by LANGMUIR, who concludes to dissociation of the hydrogen molecules from the abnormally high energy required to keep the tungsten wires in a hydrogen atmosphere at high temperature, and who tries to calculate the degree of dissociation from these energy measurements.<sup>1)</sup> On account of the insufficient accuracy of the required quantities these calculations cannot yield any but rough values. From the values of the degree of dissociation, which LANGMUIR considers the most probable, I have calculated the moment of inertia by the aid of equation 4 and 4*a*, resp. 6 and 6*a* of my preceding communication; the limits for the values for  $\log M$  found thus amount to  $-44.3$  (TETRODE and VAN DER WAALS at  $\lambda = 0$ ), and  $-45.3$  (VAN DER WAALS at  $\lambda = 20\mu$ ). From this moment of inertia the value  $8.10^{-11}$  resp.  $2.5.10^{-11}$  cm. would follow for the atom distance. The moment of inertia of hydrogen, however, is in my opinion sufficiently accurately known to justify us in rejecting these values, and in concluding that the values given by LANGMUIR, are not accurate.

Reversely it would certainly be of importance to seek an interpretation of the phenomena found by LANGMUIR, by the aid of equations 4 and 6 and of the value of the moment of inertia of hydrogen, as it is found according to other methods.<sup>2)</sup>

The chlorine dissociation has been examined at temperatures between 1700 and 2000 K. by PIER; owing to the great experimental difficulties accompanying this investigation, these values are not accurate either.<sup>3)</sup> If we calculate for this case the value of the moment of inertia, we find values for  $\log M$  varying between about  $-54$  and  $-37$ . Now we can certainly disregard the smallest values, because they are found from the determinations at the lowest temperatures, where the degree of dissociation is very small, and a small absolute error manifests itself greatly enlarged in the equilibrium constant. But also at the higher temperatures the value of  $\log M$  varies too much to allow us to draw satisfactory conclusions.

The case of the bromine dissociation is somewhat more favourable. If we apply the equations 4 and 6 to the values found by PERMAN

<sup>1)</sup> LANGMUIR, Journ. Amer. Chem. Soc. **34**. 860. (1912).

<sup>2)</sup> Cf. for the moment of inertia of hydrogen among others EINSTEIN and STERN, Ann. der. Physik. (4) **40**. 551. (1913).

<sup>3)</sup> PIER, Zeitschr. f. physik. Chemie. **62**. 417. (1908).

and ATKINSON<sup>1)</sup> we find further that the determinations at the lowest temperatures, where the degree of dissociation is very small, are useless for the calculation. If the term with  $\nu$  is omitted from equation 6, it can be brought into the following form for the bromine dissociation:

$$\frac{\sum n E_{T=0}}{4.571 T} + \log M = -\log \frac{x^2}{1-x^2} + \frac{3}{2} \log T - 38302, \quad (14)$$

in which  $x$  represents the degree of dissociation at atmospheric pressure. Application of this expression to the experimental determinations yields the following table:

TABLE VI.

$t$	$x$	2nd member of (14)	$(TC_0)_{\lambda=0}$	$\left(\frac{\Delta TC_0}{\Delta T}\right)_{\lambda=0}$
900	0.0148	-30.039	35236	-40.75
950	0.0253	-30.477	37273	-39.85
1000	0.0398	-30.845	39266	-40.75
1050	0.0630	-31.220	41304	
			mean -40.45	

The thus found value of  $-40.45$  yields  $4.10 \cdot 10^{-10}$  cm. for the radius of inertia. If the experimental determinations do not contain great errors, a very small radius of inertia follows from this calculation. And this radius would be found still smaller, if the term with  $\nu$  was taken into account. I think, however, that no great importance is to be attached to this value, because the values of the fifth column differ too much from each other, and the determinations are less numerous and less accurate than for the iodine dissociation. The accuracy is here again smaller, because the equilibrium lies strongly on one side in these determinations.

### 13. The equilibrium $2AB \rightleftharpoons A_2 + B_2$ .

When Prof. VAN DER WAALS Jr.'s considerations are applied in a perfectly analogous way to the equilibrium  $2AB \rightleftharpoons A_2 + B_2$ , we find for the dissociation constant:

$$\frac{n_{A_2} n_{B_2}}{n_{AB}^2} = e^{-\frac{\sum n E_{T=0}}{RT}} \frac{m_{A_2}^{3/2} m_{B_2}^{3/2} M_2 M_3}{m_{AB}^3 M_1^2} \frac{\left(1 - e^{-\frac{\nu_1 h}{kT}}\right)^2}{\left(1 - e^{-\frac{\nu_2 h}{kT}}\right) \left(1 - e^{-\frac{\nu_3 h}{kT}}\right)}, \quad (15)$$

<sup>1)</sup> PERMAN and ATKINSON, Z. phys. Chem. **33**, 215, 577 (1900) Cf. also: ABEGG, Handbuch **4**, 2, 233 (1913).

in which  $M_1$ ,  $M_2$ , and  $M_3$  represent the moments of inertia,  $r_1$ ,  $r_2$ , and  $r_3$  the vibrations of the molecules  $AB$ ,  $A_2$ , and  $B_2$ .

If by the aid of the entropy values of § 2 the value of  $K$  is determined we get, disregarding the term with the  $r$ -values, an identical expression. Hence the expressions of SACKUR, TETRODE, VAN DER WAALS Jr., and also those of STERN, when at least with regard to the latter it is assumed that NERNST's heat theorem is valid, yield the same result here.

With regard to the test of this expression we must remark that there occur three moments of inertia in equation 15, and that the ratio of the moments of inertia can only be determined from the equilibrium values.

The value of  $\Sigma n E_{T=0}$ , which naturally cannot be directly determined with the equilibrium  $I_2 \rightleftharpoons 2I$ , can generally be calculated here from the caloric data of BERTHELOT, THOMSEN, and others.

From equation 15 follows for the transformation energy:

$$\Sigma n E = \Sigma n E_{T=0} + \frac{N h \nu_2}{e^{kT} - 1} + \frac{N h \nu_3}{e^{kT} - 1} - 2 \frac{N h \nu_1}{e^{kT} - 1} \quad . \quad (16)$$

If we, therefore, know the  $r$ -values from the specific heats, the value of  $\Sigma n E_{T=0}$  can be determined from the thermo-chemical determination of  $\Sigma n E$ . The  $r$ -terms are generally so small that they do not cause appreciable deviations between these quantities.

At low temperatures in equation 15 the term with the frequencies has about the value 1. The material that admits of testing, now consists for a great part of determinations of electromotive forces of gas cells, in which the term of vibration may therefore be left out. Then, however, the agreement with SACKUR's expressions becomes perfect, and I can therefore refer to his paper for the testing of these determinations.<sup>1)</sup> SACKUR finds good agreement between the experimental determinations and his expressions, which are founded on the moment of inertia, which follows from the mean molecule radii ( $b$  of the equation of state, index of refraction and internal friction). At higher temperatures, however, the term with  $\nu$  asserts its influence, and we shall, therefore, have to examine it; for the sake of completeness I have inserted the values of the gas cells also in the subjoined tables.

#### 14. The equilibrium $2HCl \rightleftharpoons H_2 + Cl_2$ .

The heat of formation of  $2HCl$  from  $H_2$  and  $Cl_2$  is given by

<sup>1)</sup> SACKUR, Ann. der Physik. (4) 40 101 (1913).

THOMSEN and BERTHELOT in good agreement at 44000 cal. The specific heats of  $H_2$  and  $HCl$  differ little from 5 at room temperature; the energy of vibration is, therefore, still imperceptible here. Hence the corresponding terms with  $\nu$  can be omitted in 16. The specific heat of chlorine amounts to  $8.130 - 1.985 = 6.145$  at  $T = 616.4$  according to STRECKER (for constant volume)<sup>1)</sup>. This value corresponds to  $\lambda = 9.5 \mu$  (see equation 12). If this is substituted in equation 16, the term with  $\nu_3$  appears to have no appreciable value at room temperature either; we may, therefore, take  $\sum nE$  and  $\sum nE_{T=0}$  equal, and for the hydrochloric acid equation 15 may be transformed into:

$$\log K = -\frac{44000}{4.571 T} + \log \frac{\left(1 - e^{-\frac{\nu_1 h}{kT}}\right)^2}{\left(1 - e^{-\frac{\nu_2 h}{kT}}\right)\left(1 - e^{-\frac{\nu_3 h}{kT}}\right)} + \log \frac{M_2 M_3}{M_1^2} - 1,458 \quad (17)$$

or

$$\log \frac{M_2 M_3}{M_1^2} + \log \frac{\left(1 - e^{-\frac{\nu_1 h}{kT}}\right)^2}{\left(1 - e^{-\frac{\nu_2 h}{kT}}\right)\left(1 - e^{-\frac{\nu_3 h}{kT}}\right)} = \log K + \frac{9626}{T} + 1,458 \quad (18)$$

The experimental determinations which admit of a test of 18, are the determinations of the gas cells of DOLEZALEK<sup>2)</sup> and MÜLLER<sup>3)</sup> and the direct determination of the dissociation of LÖWENSTEIN<sup>4)</sup>.

If the values found by them are filled in in 18, we find:

T A B L E VII.

$t$	$T$	$\log K$	Second member of 18	$\log \frac{M_2 M_3}{M_1^2}$	Observer
25	298	- 33.18	0.58	0.58	MÜLLER
30	303	- 32.37	0.86	0.86	DOLEZALEK
1556	1829	- 5.772	0.95	0.70	LÖWENSTEIN

mean 0.71

1) STRECKER Wied. Ann. **17**. 102 (1882). Cf. also PIER. Zeitschr. f. physik. chem. **62** 416 (1908).

2) DOLEZALEK. Zeitschr. f. physik. Chem. **26** 321 (1898). BODENSTEIN and GEIGER. *ibid.* **49** 72 (1904).

3) MÜLLER. Zeitschr. f. physik. Chem. **40** 158 (1902). NERNST. Sitz. Ber. Preuss. Akad. 1909. 263.

4) LÖWENSTEIN. Zeitschr. f. physik. Chem. **54**. 715 (1906). The value given in the table VII has been corrected for the dissociation of chlorine into atoms. See NERNST. Zeitschr. f. Elektroch. **15** 689 (1909).

In the first two determinations the  $\nu$ -term has no perceptible influence; in the last it has. The value of the term for chlorine will certainly predominate here. If this is taken into account ( $\lambda = 9.5 \mu$ ), we find the value of column 5. When the value of  $\log \frac{M_2 M_3}{M_1^2}$  is calculated from the mean molecule radii, as they are given by SACKUR, we find 0.82, which is therefore in satisfactory agreement with the mean value 0.71. We must therefore conclude, that if the centres in  $\text{Cl}_2$  and  $\text{H}_2$  are closer together than corresponds with the mean molecule radius, the same thing is the case in about the same degree with  $\text{HCl}$ .

15. *The equilibrium*  $2 \text{HBr} \rightleftharpoons \text{H}_2 + \text{Br}_2$ .

When for  $\Sigma nE$  we substitute in 15 the value 24200 cal., which was calculated by OSTWALD from THOMSEN'S measurements<sup>1)</sup>, this equation may be transformed into:

$$\log \frac{M_2 M_3}{M_1^2} + \log \frac{\left(1 - e^{-\frac{\nu_1 h}{kT}}\right)^2}{\left(1 - e^{-\frac{\nu_2 h}{kT}}\right) \left(1 - e^{-\frac{\nu_3 h}{kT}}\right)} = \log K + \frac{5294}{T} + 1.968. \quad (19)$$

Application to the determinations of BODENSTEIN and GEIGER<sup>2)</sup> and VOGEL VON FALCKENSTEIN<sup>3)</sup> here yields:

T A B L E VIII.

$t$	$T$	$\log K$	Second member of 19	Observer
30	303	-18.43	1.01	BODENSTEIN and GEIGER
1024	1297	- 5.20	0.85	VOGEL VON FALCKENSTEIN
1108	1381	- 4.87	0.93	"
1222	1495	- 4.53	0.98	"

At  $T = 303$  the influence of the  $\nu$ -term is still imperceptible;  $\log \frac{M_2 M_3}{M_1^2}$ , therefore, amounts to 1.01 according to this determination.

From the mean molecule radii we find  $\log \frac{M_2 M_3}{M_1^2} = 1.11$  in good harmony with it.

<sup>1)</sup> OSTWALD. Allgem. Chem. II. 1, 110.

<sup>2)</sup> BODENSTEIN and GEIGER. Zeitschr. f. physik. Chem. 49, 70 (1904).

<sup>3)</sup> VOGEL VON FALCKENSTEIN. Zeitschr. f. physik. Chem. 68, 279 (1909) and 72, 115 (1910).

With regard to the observations at high temperatures it should be borne in mind that the term with  $v$  positive, because the influence of the bromine vibration will be the greatest. Hence the value of  $\log \frac{M_2 M_3}{M_1^2}$  becomes smaller than the values of the fourth column of the above table. But moreover the value for  $\log K$  has been calculated on the assumption that at the test temperatures bromine is not dissociated into atoms. From the expression of the bromine dissociation of § 12 (equation 14) it would, however, follow, that under the circumstances of these experiments the bromine is split up for a great part, and that thence a large correction is to be applied for  $\log K$ . This correction, however, makes  $\log K$  smaller, hence the value in the fourth column also becomes smaller, which would render the agreement with the first value of  $\log \frac{M_2 M_3}{M_1^2}$  still worse. I have not succeeded in bringing these determinations in satisfactory concordance with the electromotive ones. If the correction which is to be applied in VOGEL VON FALCKENSTEIN'S observations for the dissociation of bromine into atoms, was sufficiently accurately known, an attempt would be justified to get agreement between the values of  $\log \frac{M_2 M_3}{M_1^2}$  by a change in  $\Sigma nE$ . We should then have to choose a smaller value for the heat of reaction; the energy term in 19 then yields a greater decrease of the value of  $\log \frac{M_2 M_3}{M_1^2}$  at the lowest temperature than at the higher temperatures. The consequence of this would then be that the value of  $\frac{M_2 M_3}{M_1^2}$  became smaller than corresponds to the mean molecule radii. But then the value which can be derived from BERTHELOT'S observations, and which is not smaller, but greater than that of THOMSEN, would plead against this attempt.

16. *The equilibrium*  $2 HI \rightleftharpoons H_2 + I_2$ .

The value for the reaction energy having a very great influence on the value of the moments of inertia also at this equilibrium, I will try to derive this value directly from the observations themselves in an analogous way as in the iodine dissociation. This is possible here because the number of observations of the iodine hydrogen dissociation equilibrium is much greater than the bromine hydrogen equilibrium.

When in 15 we fill in the values for the masses of the reacting

molecules, and bear in mind that in HI and H<sub>2</sub> the vibration of the atoms at ordinary temperature does not yet manifest itself in the amount of the specific heats, but that this is the case for iodine, (see § 6), so that the term of vibration of the iodine molecule will be the predominating one, then with neglect of the r-terms for HI and H<sub>2</sub>, equation 15 may be transformed into:

$$\log \frac{M_2 M_3}{M_1^2} - \frac{\sum n E_{T=0}}{4.571 T} = \log K + \log \left( 1 - e^{-\frac{23h}{kT}} \right) + 2.263 \quad (20)$$

If we now fill in the value 15  $\mu$  for  $\lambda_3$  (see § 6), the observations of STEGMÜLLER (gas cells)<sup>1)</sup> and of BODENSTEIN (direct dissociation determinations)<sup>2)</sup> yield the following table: (p. 1024)

If equation 20 is written in the form:

$$C = T \log \frac{M_2 M_3}{M_1^2} - \frac{\sum n E_{T=0}}{4.571}, \quad \dots \quad (21)$$

in which  $C$  represents the value of the second member of 20, every time multiplied by the corresponding absolute temperature, then in a graphical representation, in which  $C$  is laid out as function of  $T$ , the observations must form a straight line. Then it appears graphically that a straight line can be drawn through the observations with the parameters  $\log \frac{M_2 M_3}{M_1^2} = 1,184$  and  $\frac{\sum n E_{T=0}}{4.571} = 529$ ; the observed points are then spread on both sides of this line. Then follows for the expression of the iodine hydrogen equilibrium:

$$\log K = -\frac{529}{T} - \log \left( 1 - e^{-\frac{972}{T}} \right) - 1,079 \quad \dots \quad (22)$$

It will certainly be possible to make a slight modification in the parameters without appreciably impairing the agreement between calculated and found values; it appears from the subjoined table that the errors in the observations at the lowest temperatures are pretty large, but that the expression 22 satisfactorily represents the other observations.

Dissociation determinations at high temperatures have been made by VOGEL VON FALCKENSTEIN<sup>3)</sup>. They have been carried out by measurement of the partial pressure of the hydrogen, use being made of the permeability of platinum to this gas, and of its impermeability to the other gases. The equilibrium constants, which have

1) STEGMÜLLER. Zeitschr. f. Elektrochem. **16**, 85 (1910).

2) BODENSTEIN. Zeitschr. f. physik. Chem. **29**, 295 (1899).

3) loc. cit.

TABLE IX.

$t$	$T$	$\log K$	$\nu$ term	Second member of 20	Observer
31.6	304.6	- 2.925	- 0.018	- 0.680	STEGMÜLLER
55.2	328.2	- 2.692	- 0.023	- 0.452	"
81.6	354.6	- 2.416	- 0.029	- 0.182	"
280	553	- 1.931	- 0.082	+ 0.250	BODENSTEIN
300	573	- 1.905	- 0.088	0.270	"
320	593	- 1.878	- 0.094	0.291	"
340	613	- 1.851	- 0.100	0.312	"
360	633	- 1.823	- 0.105	0.335	"
380	653	- 1.794	- 0.111	0.358	"
400	673	- 1.765	- 0.117	0.381	"
420	693	- 1.735	- 0.123	0.405	"
440	713	- 1.705	- 0.128	0.430	"
460	733	- 1.675	- 0.134	0.454	"
480	753	- 1.644	- 0.140	0.479	"
500	773	- 1.612	- 0.145	0.506	"
520	793	- 1.580	- 0.151	0.532	"

TABLE X.

$T$	$\log K$ (found)	$\log K$ (calc.)	$T$	$\log K$ (found)	$\log K$ (calc.)
304.6	- 2.925	- 2.798	653	- 1.794	- 1.778
328.2	- 2.692	- 2.668	673	- 1.765	- 1.748
354.6	- 2.416	- 2.542	693	- 1.735	- 1.719
553	- 1.931	- 1.954	713	- 1.705	- 1.693
573	- 1.905	- 1.914	733	- 1.675	- 1.667
593	- 1.878	- 1.877	753	- 1.644	- 1.642
613	- 1.851	- 1.842	773	- 1.612	- 1.618
633	- 1.823	- 1.810	793	- 1.580	- 1.595

been inserted in the above table in the fourth column, were calculated from the values of this pressure.

TABLE XI.

<i>t</i>	<i>T</i>	<i>x</i>	<i>log K</i>	<i>log K</i> (corr.)	<i>log K</i> (from 22)
1022	1295	0.329	- 1.221	- 1.368	- 1.210
1217	1490	0.3755	- 1.044	- 1.384	- 1.115

The values of the fourth column have been calculated on the assumption that all the iodine is present as  $I_2$ ; this now is certainly not the case according to the determinations of the iodine dissociation (see § 5). At these temperatures the iodine has already perceptibly been split up into atoms, and specially at the low iodine tension of these experiments the splitting up will be great. Through the correction which is to be applied for this, *log K* of column 4 becomes smaller.

Let us suppose the iodine to be partially split up into atoms (degree of splitting  $y$ ), then the total iodine pressure is not equal to the hydrogen pressure, but  $1 + y$  times greater. Let us call the hydrogen pressure  $P_{H_2}$ , the total pressure  $P$ , then we have for the partial tensions of hydrogen, iodine atoms, iodine molecules and iodine hydrogen:

$$P_{H_2}, \quad 2y P_{H_2}, \quad (1 - y) P_{H_2} \quad \text{and} \quad P - (2 + y) P_{H_2}.$$

Hence the equilibrium constant for iodine hydrogen becomes:

$$K_{HI} = \frac{P_{H_2}^2(1-y)}{[P - P_{H_2}(2+y)]^2} \quad \dots \quad (23)$$

and that for the iodine dissociation expressed in partial pressures:

$$K_{I_2} = \frac{4y^2}{1-y} P_{H_2} \quad \dots \quad (24)$$

Now from the equation for the iodine dissociation (equation 13) follows for the equilibrium constant (in partial pressures; pressure unity the atmosphere):

$$\left. \begin{array}{l} T = 1295 \quad \log K_{I_2} = - 0.668 \\ T = 1490 \quad \log K_{I_2} = + 0.148 \end{array} \right\} \dots \quad (25)$$

If we now introduce the values of 25 and the found values of  $P_{H_2}$  into 24,  $y$  may be calculated from it. This value of  $y$  substituted in 23, yields the values *log K* (corr.) of table XI. When

the value of  $\log K$  is calculated from 22, we get the values of the sixth column of table XI, which appreciably differ from those of the fifth column. This deviation can, however, be accounted for by this that the terms with  $\nu$  of  $HI$ , and possibly also those of  $H_2$ , play a part at these high temperatures; the term with  $HI$  will render the value of  $\log K$  according to 22 smaller. The iodine vibration which prevails at low temperatures, will also continue to do so at high temperatures. The value of the iodine term amounts to  $-0.277$  at  $T=1295$ , and to  $-0.319$  at  $T=1490$ ; the term, therefore, which occurs in expression 22 through the vibration of the atoms in  $HI$ , remains below this value; and in this way an agreement may be probably arrived at, as the discrepancies between the values of the fifth and the sixth columns are smaller than the mentioned ones. Moreover some variation is still possible in the choice of the parameters of the straight line (equation 21).

The equation 22, which is accordingly in satisfactory agreement with all the determinations of the iodine hydrogen equilibrium, yields the value 1,184 for  $\log \frac{M_2 M_3}{M_1^2}$ . If from the mean molecule radii, as they are given by SACKUR, the value of the expression mentioned is calculated, we find 1,21 which is therefore in good agreement with the preceding one.

From formula 22 the value 2530 cal. follows for  $\sum n E_{T=300}$ , this value differs but little from that used by NERNST in his calculations<sup>1)</sup>; most of the data which can be derived from direct caloric determinations, are useless.

17. From the calculations of the dissociation equilibria of the three halogen hydrogens we come therefore to the conclusion that the quotient of the moments of inertia agrees with that calculated from the mean molecule radii.

This conclusion, at which SACKUR by the aid of his expressions had arrived already before, but which was only meant to be roughly valid, appears also to be in good harmony with Prof. VAN DER WAALS Jr.'s expression, in which the vibrations of the atoms are taken into account.

*Amsterdam, Dec. 1914. Anorg. Chem. Lab. of the University.*

<sup>1)</sup> Zeitschr. f. Elektrochem. 15, 687 (1909).

**Chemistry.** — “*The replacement of substituents in benzene derivatives.*” By Prof. HOLLEMAN:

(Communicated in the meeting of December 30, 1914).

In close connexion with the problem of the introduction of substituents in aromatic compounds exists another: that of the replacement of substituents already present, for after all the introduction is really also a substitution, namely of hydrogen. It, therefore, appeared to me desirable to also take in hand the study of the replacement, in addition to my researches on the introduction of substituents.

Some generalities on this subject are to be found in every textbook on organic chemistry. We know that the substituent in monosubstituted benzene derivatives is very difficult of substitution; that in the disubstituted derivatives it is the combination of halogen and the nitro-group in which halogen is replaceable if the groups are *o* or *p* in regard to each other; that in compounds  $C_6H_3ABC$  replacement also occurs if the substituents consist of halogen, nitro, carboxyl, cyanogen or the sulpho-group (with this understanding, however, that except in a very few cases, there is no such thing as  $A=B=C$ ); finally that also in the higher substituted benzene derivatives instances of replacement occur. As interacting substances have been employed almost exclusively alcoholates, ammonia and amines. In order to obtain a better insight in this problem the compounds  $C_6H_5X$  could be passed over; on the other hand the literature on the compounds  $C_6H_4AB$  and  $C_6H_3ABC$  had to be studied more closely.

Statistically, this yielded the following results: If we consider the compounds  $C_6H_4AB$  and  $C_6H_3ABC$ , in which also A, B, and C may be equal, and if for these substituents we take the following 14: F, Cl, Br, J,  $NO_2$ ,  $SO_3H$ , Alkyl (Aryl),  $CO_2H$ ,  $NH_2$  (amine), OH (O Alk), CN, NO, CHO, COR, we can derive from  $C_6H_4AB$   $\frac{n(n+1)}{1.2} = \frac{14 \times 15}{2} = 105$  repeated combinations all of which can form three isomerides; hence a total of 315 cases (included  $A=B$ ).

Of  $C_6H_3A_3$  are possible 14 combinations; 3 isomerides of each = 42 cases.

Of  $C_6H_3A_2B$  are possible  $n(n-1) = 14 \times 13 = 182$  combinations; each can occur in 6 isomerides, thus representing 1092 cases.

Of  $C_6H_3ABC$  are possible  $\frac{n(n-1)(n-2)}{1.2.3} = \frac{14 \times 13 \times 12}{6} = 364$  combinations; 10 isomerides of each = 3640 cases.

For all compounds  $C_6H_3ABC$  with repetitions this gives a total of  $42 + 1092 + 3640 = 4774$  cases. <sup>1)</sup>

If now we inquire how many of these theoretically possible isomerides have been tested as to the replacement of their substituents we get the following information :

Of the 315 possible isomerides  $C_6H_4AB$  (incl.  $A = B$ ) 130 have been tested as to substitution and the results are distributed over 214 papers.

For the 4774 possible isomerides  $C_6H_4ABC$  (incl.  $A_2B$  and  $A_3$ ) these figures are : of 232 compounds the substitution has been described in 360 papers.

This shows that only a very small portion of the possible compounds  $C_6H_4AB$  and  $C_6H_3ABC$  has been tested as to the replacement of their substituents ; it only amounts to fully 7 %.

Hence, it is hardly to be expected that from this general conclusions might be drawn even if all published cases of substitution were suitable for the object in view. But this is by no means the case. After a careful study of the above named  $214 + 360 = 574$  articles we even arrive at the disappointing result that this vast material is almost valueless for a closer study of the substitution. For in such a study we not only want to know in what particular combinations substitution can occur, but also how this takes place under the same conditions. For only then will it be possible to compare mutually the substitution in the different groups and thus obtain a better insight by investigating this problem. And exactly in this regard, the material at disposal almost entirely forsakes us.

The reason is obvious. The experiments on substitution carried out up to the present have always been executed with quite a different purpose and were not intended for a systematic study of this problem. Hence, the work was conducted hardly ever under comparable conditions. The only results obtained up to the present is that we know that in a comparatively limited number of cases substitution is possible. From this we may predict with great probability that there is a possibility of substitution in a number of other cases. If, for instance we know that in chloronitrobenzenes with one or several chlorine atoms or nitro-groups the chlorine is mobile, it is to be considered as very probable that this will also be the case with the other halogen-nitrobenzenes of the same structure.

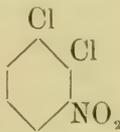
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<sup>1)</sup> Our fellow member Hk. DE VRIES was kind enough to furnish me with the formulae used here.

The first thing to do here must be an orientating investigation to see which combinations of substituents give rise to the mobility of one or more of the same when they are examined under exactly the same conditions. It is, of course, impossible to include all the 5089 compounds  $C_6H_4AB$  and  $C_6H_3ABC$ , of which 4727 have never as yet been tested in any way as to substitution, and of which a good many are sure to be still unknown, in such an orientating investigation. A choice had to be made. It appeared to me desirable to start with a gauging of the intricateness of this problem by (1) measuring in a complete set of isomerides the velocity of the transformation; (2) to do this for two different substances acting thereon; (3) to execute this at different temperatures. From this would then be shown in the first place the influence of the position of the substituents. In the second place it would show whether there exists a definite ratio between the constants when working with different reagents and in the third place whether that ratio also remains permanent at various temperatures. If this really were so this would cause a considerable simplification of the problem. We then would only have to work at a well chosen temperature and with a ditto reagent to generally obtain comparable velocity constants.

The subjoined investigation of Dr. DE MOOIJ briefly described here has taught, however, that the said ratio does not exist either for temperature or for difference in reagent. This shows that the substitution problem possesses such a degree of complicateness that an accurate insight therein is still a matter of the distant future.

As objects for the research of Dr. DE MOOIJ were chosen the six isomeric nitrodichlorobenzenes. All these are comparatively readily

prepared in quite a pure condition; only for the isomeride  an easier process of preparation had to be discovered and was successfully worked out.

He brought these six isomerides in contact with absolute-methyl-alcoholic solutions of sodium methoxide and of diethylamine, isolated all the products of transformation and determined the velocity constants at three different temperatures. The symmetric isomeride gave with methoxide a complicated reaction product consisting presumably of azoxycompounds; diethylamine did not act on it on heating for seven days at  $110^\circ$ , so that with this isomeride no velocity measurements could be carried out.

The three chloronitrobenzenes, likewise the three dichlorobenzenes were also treated in the same manner when it appeared, however, that the last named did not react with diethylamine even at  $180^\circ$ , but they reacted with  $\text{NaOCH}_3$ . The disubstituted products were tested to ascertain whether from the velocity constants of their transformations, those of the compounds  $\text{C}_6\text{H}_2\text{Cl}_2\text{NO}_2$  could be deduced. Also this did not appear to be so.

From the results obtained by Dr. DE MOOR the following will be communicated. In all the cases investigated only chlorine was replaced, not the nitro-group.

1. *Chloronitrobenzenes*. Of these was measured the reaction velocity with sodium methoxide and with diethylamine both in absolute methylalcoholic solution. Whereas with the first named compound the velocity constant for the p-compound was found greater than that of the o-compound, this was just the reverse with diethylamine. The reaction with diethylamine proceeds here as well as in all other cases much more slowly than with methoxide. (see table III).

2. *Dichlorobenzenes*. These were heated with sodium methoxide at  $175$ — $176^\circ$  when one Cl-atom was replaced by OH, as the solution was not quite anhydrous. For the constants (time in hours) was found, when 1 mol. of dichlorobenzene was made to react with 5 mols. of methoxide:

TABLE I.

$\text{C}_6\text{H}_4\text{Cl}_2$	K	Ratio
ortho	0.0382	3.35
meta	0.0506	4.44
para	0.0114	1

from which is shown the very remarkable result that the *m*-compound is the one most rapidly converted, a fact that was quite unexpected.

3. *Nitrodichlorobenzenes*. The most successful measurements obtained here are those with sodium methoxide as the values of K at different reaction periods were found to be pretty constant. In the measurements with diethylamine this was only the case with the isomerides 1,2,4 and 1,2,5 ( $\text{NO}_2$  on 1); with the others the value K diminished as time proceeded. Particularly interesting was the behaviour of the

isomerides 1,2,4 and 1,2,6. In the first compound, at the interaction of  $\text{NaOCH}_3$ , both chlorine atoms appeared to be already mobile at  $85^\circ$ , but contrary to what takes place with monochloronitrobenzenes, the chlorine atom on 2 is being replaced first. The consequence was that at this temperature the constant became greater as time proceeded. At  $25^\circ$  and  $50^\circ$ , however, the reaction with the p-Cl-atom in regard to that of the o-Cl-atom was so retarded that very concordant values were now found for K. With diethylamine, only the o-Cl-atom was mobile.

In the isomeride 1,2,6 the two Cl-atoms were situated in o-positions in regard to the nitro-group. Nevertheless only one Cl-atom could be made to react with  $\text{NaOCH}_3$  at  $85^\circ$ ; and the same likewise with diethylamine at  $150^\circ$ .

The subjoined table II gives a survey of the measured velocity

TABLE II.

Isomeride	$25^\circ$	$50^\circ$	$85^\circ$	$110^\circ$
1, 2, 3	—	—	1.74	14.3
1, 2, 4	0.030	0.628	19.41	—
1, 2, 5	0.0063	0.121	3.93	33.0
1, 2, 6	—	—	0.135	1.34
1, 3, 4	0.033	0.601	17.42	—
1, 2	—	—	0.369	3.09
1, 4	—	—	1.39	11.45

constants with Na-methoxide. The figures in heavy type indicate the Cl-atom that is being replaced.  $\text{NO}_2$  on 1. Time in hours. On 1 mol. of nitrodichlorobenzene one mol. of methoxide was employed. Both were in about gas-concentration. From this we notice that the position of the groups in regard to each other exerts a very great influence on the velocity of the reaction. If we put the reaction velocity of 1,2,4 at  $85^\circ = 100$ , that of 1,2,6 will then be only 0.7. also in the case of the other vicinal isomeride the reaction constant is very small, namely only 8.9 for 1, 2, 4 = 100.

If we compare the reaction constant of o-chloronitrobenzene with that of the nitrodichlorobenzenes in which also one of the Cl-atoms is situated in the o-position in regard to  $\text{NO}_2$ , the introduction of a second chlorine atom then appears to considerably increase that constant, except in the case where the second Cl-atom occupied the

position 6. Likewise the reaction constant of 1,3,4 is considerably greater than that of 1,4.

The reaction constants with diethylamine were determined with the proportion of 1 mol. of nitro-dichlorobenzene to 2 and to 10 mols. of diethylamine, which did not yield quite the same values for those constants. In table III the values found are united. The time has again been recorded in hours.  $\text{NO}_2 = 1$ .

TABLE III.

Isomeride	85°		110°	
	1 : 2	1 : 10	1 : 2	1 : 10
1, 2, 3	0.0023	0.0016	0.0094	0.0073
1, 2, 4	0.025	0.027	0.12	0.095
1, 2, 5	0.0068	0.0067	0.032	0.023
1, 2, 6	—	0.00024	—	0.0011
1, 3, 4	0.0052	0.0044	0.020	0.017
1, 2	—	0.0014	—	0.0053
1, 4	—	0.00065	—	0.0024

The impression made by this table is in the main the same as that of table II. Also here the reaction constants of the two vicinal isomerides are considerably smaller than those of the other nitro-dichlorobenzenes and that for the isomeride 1,2,6 is also the smallest. The isomeride 1,2,4 has also here the greatest reaction constant but now this is not followed up by that of 1, 3, 4 as in the case of the methoxide reaction; presumably this is connected with the fact that the reaction constant for 1,4 with diethylamine is smaller than that of 1,2, whereas with methoxide this is just the reverse. That, however, also in the other cases which run parallel, there can be no question of a constant relation between the reaction constants with methoxide and with diethylamine may be seen at once from table IV. p. 1033.

Not only are the figures in a same column very divergent, but the corresponding figures of the two columns differ very much; those at 110° are all about twice greater than those at 85°, which indicates that the reaction velocity for methoxide increases much more rapidly with the temperature than that for diethylamine.

Table V gives the figures as to the influence of the temperature on the reaction constant. Whereas the ratios for methoxide on the

TABLE IV.

Isomeride	$K_{\text{NaOCH}_3} : K_{\text{amine}}$	
	$T = 85^\circ$	$T = 110^\circ$
1, 2, 3	892	1744
1, 2, 4	747	—
1, 2, 5	582	1200
1, 2, 6	563	1218
1, 3, 4	3629	—
1, 2	264	583
1, 4	2138	4771

one side and for diethylamine on the other side agree fairly well, this is by no means the case for the two reagents mutually.

TABLE V. Na-methoxide.

Isomeride	$K_{25} : K_{50} : K_{85} : K_{110}$	$K_{85} : K_{110}$	Diethylamine (1 : 10)
			$K_{85} : K_{110}$
1, 2, 3	—	1 : 8.2	1 : 4.4
1, 2, 4	1 : 20.9 : 647	—	1 : 3.5
1, 2, 5	1 : 19.2 : 624 : 5238	1 : 8.4	1 : 3.4
1, 2, 6	—	1 : 10	1 : 4.6
1, 3, 4	1 : 18.2 : 528	—	1 : 3.9
1, 2	—	1 : 8.4	1 : 3.8
1, 4	—	1 : 8.2	1 : 3.7

Summarising we arrive at the following conclusions:

1. The number of cases of replacement of substituents in the compounds  $C_6H_4AB$  and  $C_6H_3ABC$  quoted in the literature is small in comparison with the number of possible cases.

2. The data of the literature are of little value for a systematic research as to the substitution problem as they have rarely been obtained under comparable conditions.

3. From the study of the replacement of chlorine in the three dichlorobenzenes, the three chloronitrobenzenes and the six nitrodichlorobenzenes by  $OCH_3$  and  $N(C_2H_5)_2$ , it is shown:

a. that the replacement of the halogen is largely dependent on the position of the substituents:

b. that it is dependent on the reacting agent.

c. that the influence of the temperature on the extent of the velocity constants is different for the two reactions, although fairly equal for the different isomerides in each reaction.

A more detailed communication of the above will appear in the *Recueil*.

Amsterdam, Dec. 1914.

Org. Chem. Lab. University.

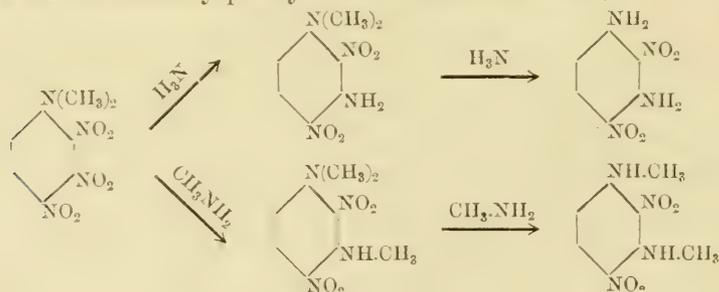
**Chemistry.** — “On the interaction of ammonia and methylamine on 2,3,4-trinitrodimethylaniline.” By Prof. VAN ROMBURGH and Miss D. W. WENSINK.

(Communicated in the meeting of December 30, 1914).

3,4,6.- as well as 2,3,4.-trinitrodimethylaniline, contains a mobile nitro-group (in the position 3) which is readily substituted in the interaction of ammonia and amines<sup>1)</sup>. The mobility of that group in the second mentioned product is, however, considerably greater, as was to be expected. If, for instance we pour strong alcoholic ammonia on the 2,3,4.-trinitrodimethylaniline melting at 154°, the nitro-group gets substituted by the amino-group already at the ordinary temperature, whereas the other product melting at 196° does not exhibit any reaction whatever in these circumstances and requires heating to enable the reaction to take place.

If, however, we heat the compound melting at 154°, or the 2,4.-dinitro-3-aminodimethylaniline generated thereof by ammonia, in a sealed tube at 125° with alcoholic ammonia, the dimethylaminogroup appears to become substituted in a remarkable manner by amino, with formation of 2,4.-dinitro-1,3.-phenylenediamine.<sup>2)</sup>

In a perfectly analogous manner reacts methylamine in which, case 2,4.-dinitrodimethylphenylenediamine is formed;



<sup>1)</sup> VAN ROMBURGH, Verslagen Kón. Akademie Amsterdam Febr. 1895.

<sup>2)</sup> In the said paper it is stated that indeed derivatives of m-phenylenediamine are formed.

If, for instance, we dissolve 0.5 gram of 2.3.4.-trinitrodimethylaniline in alcohol and add to the solution a few c.c. of strong alcoholic ammonia a beautiful pale yellow product crystallizes after a short time, which when recrystallised from acetone melts at 162°.

The nitrogen determination gave 24.70 and 24.52% N.  
calculated for  $C_6H_2(NO_2)_2 N(CH_3)_2 NH_2$  24.6% N.

If, however, we heat this product (or the original substance melting at 154°) for some hours with alcoholic ammonia in a sealed tube at 125°, we find in the tube after cooling an abundant quantity of a substance crystallizing in brownish needles, which dissolves with great difficulty in the ordinary solvents. By recrystallisation from boiling methyl salicylate it could be obtained in beautiful pale brown or orange needles, which get decomposed at about 250°<sup>1)</sup>.

The elementary analysis gave the following result:

C 36,22%, H 3,55%, N 28,18%; calculated for  $C_6H_2(NO_2)_2 \cdot (NH_2)_2$ :  
C 36,36%, H 3,01%, N 28,28%.

In the original mother-liquor of the brown needles in the tube, the presence of dimethylamine could be demonstrated. To ascertain this, it was acidified with hydrochloric acid and evaporated to dryness. The residue — mixture of ammonium chloride and dimethylamine hydrochloride — was extracted with absolute alcohol. After distilling off the alcohol, there remained a little of a salt which, after being washed with absolute alcohol to remove traces of nitro-compound, was decomposed by boiling with alcoholic potassium hydroxide. The distillate gave with 1-bromo 2.4-dinitrobenzene, yellow crystals of 2.4.-dinitrodimethylaniline m.p. 87°, thus demonstrating the presence of dimethylaniline.

The 2.3.4.-trinitrodimethylaniline yields with methylamine in alcoholic solution after a while yellow crystals of 2.4.-dinitro 3-methylaminodimethylaniline m.p. 125°.

Nitrogen determination: Found 23.32% N.

Calculated for  $C_6H_2(NO_2)_2 NHCH_3 N(CH_3)_2$  23.35% N.

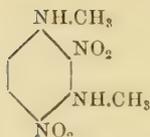
From this is formed on heating with methylamine at 125° in a sealed tube, a substance melting at 169°.

Nitrogen determination: Found 25.0%; calculated for  $C_6H_2(NO_2)_2 (NHCH_3)_2$  24.8% N.

This compound already prepared by BLANKSMÄ<sup>2)</sup> has the structural formula:

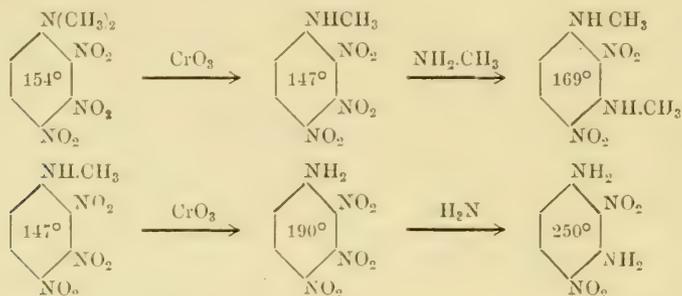
<sup>1)</sup> BARR, B. 21, 1545 (1888).

<sup>2)</sup> Rec. 27, 54 (1908).



This could further be proved by carefully oxydising the trinitro-compound (m.p.  $154^{\circ}$ ) with chromic acid in acetic acid solution, which yields the monomethyl compound melting at  $147^{\circ}$ . This gives with alcoholic methylamine-solution the *m*-phenylene-derivative melting at  $169^{\circ}$ .

A continued oxidation with chromic acid yields from the trinitro-compound m.p.  $154^{\circ}$ , a 2,3,4.-trinitroaniline (m.p.  $190^{\circ}$ ), which on treatment with ammonia gives the above cited 2,4.-dinitrophenylenediamine.



*Utrecht.*

*Org. Chem. Lab. Univ.*

**Chemistry.** — “*The influence of the hydration and of the deviations from the ideal gas-laws in aqueous solutions of salts on the solidifying and the boiling points.*” By Dr. C. H. SLUITER. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of December 30, 1914).

When, according to VAN 'T HOFF, we determine the irrationality coefficient (factor  $i$ ) of good electrolytes in the well-known manner with the telephone bridge of KOHLRAUSCH, for different solutions from the formula  $i = 1 + (n-1)\alpha$ , in which  $n$  represents the number of ions that can be yielded by one molecule, and  $\alpha$  the dissociation degree  $= \frac{A_V}{A_\infty}$  ( $A$  = equivalent conductivity power), this appears to fairly increase with the growing dilution until almost the theoretical limit has been attained.

If by other means, namely by measuring the depression of the solidifying point, or the rise in the boiling point of the solutions, we try to determine, approximately the value of  $i$  according to the formula:

$$i = \frac{\text{Observed depression S.p. or rise in B.p.}}{\text{Molecular depression S.p. or rise in B.p.} \times c'}$$

in which  $c'$  represents the number of gram-mols per 1000 grams of water, the values thus found, particularly in the case of concentrated solutions appear to agree very badly with the first named ones.

Two different causes can be adduced for these divergencies. First, the hydrations of the salt molecules and of their ions, owing to which a part of the water has been rendered inactive as a solvent. Hence, in the last formula a smaller value will be found for  $c'$  than it would have been if the salt had been really calculated on 1000 grams of solvent. The calculated value of  $i$  will thus be greater than it would have been without hydration. At high concentrations the amount of solvent withdrawn as water of hydration will be larger than at low concentrations, so that the influence on  $i$  will be most pronounced in the first case. Also, strongly hydrated salts such as  $\text{MgCl}_2$  and  $\text{CaCl}_2$  will exhibit greater differences of  $i$  than the but little hydrated ones such as  $\text{NaCl}$  and  $\text{KCl}$ .

The second cause of the divergencies lies in the relative applicability of the so-called "ideal gas-laws". When, according to VAN DER WAALS, the influence of the factors  $a$  and  $b$  on the gas pressure also applies to the osmotic pressure of the solutions, their solidifying and boiling points will also be affected thereby. We may compare solutions of salts to gases of high molecular weight because the mass of hydrated particles will be comparatively larger. With concentrations of about one gram-mol. per litre we may then expect that the factor  $b$  (volume of the particles) will exert a stronger influence than the factor  $a$  (proportional to the mutual attraction of the particles). The osmotic pressure, therefore also  $i$  will then be greater than one would expect it to be without those factors. At these large concentrations the hydration and the last named circumstance thus act on  $i$  in the same direction.

When at smaller concentrations,  $a$  becomes predominant, the osmotic pressure, hence also  $i$ , will become smaller than would be the case according to the ideal gas-laws. Now, as a rule, the question is whether  $a$  can overcome not only the influence of  $b$  but also that of the hydration of some kind of salt, so that  $i$  really becomes smaller than would be the case without one of these perturbing factors.

In the determination of  $A$  we are only concerned with the number of ions present in a certain volume of the solution so that the said perturbing factors exert no influence on the calculation of  $i$ . The relation  $\frac{A_V}{A_z}$  therefore indicates the actual value of  $i$  when  $V$  represents the reciprocal value of the number of gram-mols per 1000 cc. of solution.

I have endeavoured to ascertain, by the measurement of  $A$  the depression of the solidifying point and the rise in the boiling point at equal concentrations and temperatures, in how far these considerations are in agreement with the result of  $i$  in the case of NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub>. The arrangement of the experiments did not admit of making direct experiments at equal concentrations. I have, therefore approximated the values of  $i$  as accurately as possible by graphic interpolation. Properly speaking I ought to have determined  $A$  at the solidifying and boiling points of the solution instead of at 0° and 100°. As, however, the change of  $i$  with the temperature is very slow, this correction would not counterbalance the inaccuracies which would then be introduced owing to the great experimental difficulties.

I have also occupied myself with the calculation of  $i$  from saturated vapour determinations of saline solutions, were we can expect the same divergencies as in the dynamic determinations. Notwithstanding detailed and laborious experiments I have not succeeded in obtaining, in this manner, results sufficiently accurate for controlling the above mentioned values of  $i$ . I will only mention that  $i$ , when accurately determined within one decimal, gave the same results with the statical and the dynamical method.

In the "*Chemisch Weekblad*" (1915) will appear a more elaborate description of the apparatus employed by me and the corrections applied for the calculation of  $i$ , whilst the agreement and the differences of my results with those of other observers will also be discussed.

The following points of a more general importance, I wish to mention here.

The manner in which the conductivity power of the water, used in the  $A$  determinations, is computed is generally carried out by multiplying the specific conductivity power of the water with the dilution of the solution expressed in cc.

This empirical method, however, keeps no account with the position of the sliding contact on the measuring bridge. The following deduction may demonstrate, however, that this position exerts a strong influence on the correction to be applied. Suppose:

$W_O$  = resistance of the *solution*.

$W_B$  = comparison resistance on the *bridge*.

$W_W$  = resistance of the "conductivity *water*".

$W$  = corrected resistance of the solution in case the water possessed an infinitely great resistance.

If we assume that the conductivity power of the water is independent of the nature of the solution (as will be certainly the case with neutral salts) we have:

$$\frac{1}{W_W} + \frac{1}{W} = \frac{1}{W_O} \quad \text{or} \quad \frac{1}{W} = \frac{1}{W_O} - \frac{1}{W} \quad \dots \quad (1)$$

If we call the parts of the bridge wire, when the solution is shunted in  $a$  and  $b$  and those when the water only is shunted in  $c$  and  $d$  we have:

$$\frac{W_O}{W_B} = \frac{b}{a} \quad \text{or} \quad \frac{1}{W_O} = \frac{a}{b} \times \frac{1}{W} \quad \dots \quad (2)$$

and

$$\frac{W_W}{W_B} = \frac{d}{c} \quad \text{or} \quad \frac{1}{W_W} = \frac{c}{d} \times \frac{1}{W_B} \quad \dots \quad (3)$$

Substitution of (2) and (3) in (1) gives:

$$\frac{1}{W} = \frac{1}{W_B} \left( \frac{a}{b} - \frac{c}{d} \right) \quad \dots \quad (4)$$

If we put  $x$  the correction to the left, hence the diminution of  $a$ , which must be applied in the case when the water had an infinitely great resistance, we find in a similar manner:

$$\frac{1}{W} = \frac{a-x}{b+x} \times \frac{1}{W_B} \quad \dots \quad (5)$$

Substitution of (4) in (5) gives:

$$\frac{a-x}{b+x} = \frac{a}{b} - \frac{c}{d} \quad \text{or} \quad \frac{a-x}{b+x} = \frac{ad-bc}{bd}, \quad \text{hence} \quad x = \frac{b^2c}{d(a+b)-bc}.$$

If  $L = a + b = c + d =$  length of the bridge wire and if we neglect  $bc$  in regard to  $dL$  we have:  $x = c \times \frac{b^2}{Ld} = c \times \frac{b^2}{L(L-c)}$ .

If, herein we again neglect  $Lc$  in regard to  $L^2$  we get:

$$x = c \times \left( \frac{b}{L} \right)^2.$$

Consequently the further the sliding contact is situated towards the right, the smaller will be the corrections to be applied. In my measurements  $W_B$  was always chosen in such a manner that  $b$  was as small as possible without the telephone minima becoming less sharp. Not a single other observer appears to have applied this

correction in this manner, which, with great dilutions, can cause a difference in the value of  $A$  of several percentages. When now we represent their results of  $A$ , graphically as a function of the logarithm of the dilution, the curved lines in the vicinity of  $V = 2000$  and higher often exhibit very peculiar bends so that sometimes the graphical approximation of  $A_\infty$  becomes impossible. The curved lines deduced from my results all appear to run asymptotically with a line parallel to the dilution axis, as required by theory.

The approximation of  $A_\infty$ , particularly at  $100^\circ$ , is rather uncertain, because with very great dilutions the above described correction method for the conductivity water also fails. In order to get comparable results, I have applied the empirical method of BREDIG<sup>1)</sup> and of NOYES<sup>2)</sup> taking  $A_\infty = A_{1000} + 2,5 N$  at  $25^\circ$  ( $N =$  product of the valencies of anion and cation). I have chosen the coefficient of  $N$  at  $0^\circ$  so much smaller and at  $100^\circ$  so many times larger as the proportional decrease and increase of  $A_{1000}$  amounts to at those temperatures.

In the measurements at  $100^\circ$  which were carried out in a steam-bath, the solution being kept under a pressure of 3 atm. to prevent evolution of vapour at the electrodes, a correction had to be applied for the influence of the barometer indication on the steam-temperature. For this purpose the temperature coefficient of  $A$  of the different salts as determined by JONES<sup>3)</sup> between  $0^\circ$  and  $65^\circ$ , was used with a proportional reduction to  $100^\circ$ .

Here follow the thus corrected results of  $i$  at different dilutions ( $V$ ) at  $0^\circ$  and  $100^\circ$ . For each measurement the concentration at  $15^\circ$  was determined separately and in this way eventual errors caused by pipetting off and delivering into the measuring vessel were avoided.

The depression of the solidifying points was determined according to the method of ROBERTSON and WALKER<sup>4)</sup> in which corrections for the influence of the radiation and for the slowness with which the temperature exchange takes place, are done away with. The liquid siphoned off from the ice-saltsolvent mixture was rapidly brought to the temperature of the room and titrated. The thermometer in the DEWAR vessel remained constant for a considerable time when this vessel was properly surrounded by ice.

The concentrations all relate to a temperature of  $15^\circ$ .

1) Zs. phys. Chem. **13**, 191. (1894).

2) Technol. Quart. **17**, 293 (1904).

3) Carnegie Inst. of Washington, publ. **170** (1912).

4) Proc. Royal Soc. **24**, 363 (1902).

V	$\Delta 0^\circ$	$i 0^\circ$	$\Delta 100^\circ$	$i 100^\circ$
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*Sodium chloride*

1	48.41	1.7191	219.3	1.6094
2	51.53	1.7656	242.4	1.6736
4	54.28	1.8063	260.7	1.7244
10	57.72	1.8576	283.1	1.7868
20	60.04	1.8921	298.8	1.8305
40	61.81	1.9183	315.2	1.8760
100	63.47	1.9430	331.5	1.9210
400	65.32	1.9703	346.3	1.9625
1000	65.82	1.9777	351.8	1.9777
2000	66.04	1.9811	355.0	1.9865
$\infty$	67.32	2	359.8	2

*Magnesium chloride.*

1	68.02	2.0552	306.2	1.8860
2	77.03	2.1950	373.8	2.0816
4	85.71	2.3296	430.3	2.2452
10	96.50	2.4970	491.9	2.4234
20	104.4	2.6196	534.4	2.5462
40	110.6	2.7156	567.2	2.6416
100	117.0	2.8152	611.8	2.7702
400	123.3	2.9126	657.1	2.9016
1000	125.9	2.9532	675.0	2.9532
2000	127.1	2.9716	680.5	2.9690
$\infty$	128.9	3	691.1	3

$\Delta 0^\circ$	$i 0^\circ$	$\Delta 100^\circ$	$i 100^\circ$
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*Potassium chloride.*

63.83	1.7773	267.1	1.6704
66.41	1.8089	286.9	1.7201
68.69	1.8366	306.4	1.7686
71.50	1.8709	329.2	1.8262
73.52	1.8954	343.8	1.8628
75.44	1.9187	361.3	1.9067
77.46	1.9432	374.1	1.9389
79.63	1.9699	385.9	1.9685
80.61	1.9817	391.0	1.9813
81.00	1.9865	392.7	1.9856
82.11	2	398.5	2

*Calcium chloride.*

76.33	2.1128	326.2	1.9356
85.02	2.2392	394.3	2.1308
93.10	2.3570	445.7	2.2786
103.2	2.5042	506.1	2.4518
110.5	2.6108	546.2	2.5668
116.8	2.7030	587.8	2.6838
123.8	2.8048	621.9	2.7838
131.3	2.9144	664.5	2.9060
134.2	2.9562	682.1	2.9566
135.0	2.9680	686.2	2.9680
137.2	3	697.4	3

For the calculation of the number of gram-mols per 1000 grams of water the formula  $c' = \frac{1000 c}{1000d - cM}$  was used, in which  $c$  represents the directly-titrated concentration,  $d$  the sp. gr. of the solution and  $M$  the molecular weight of the salt.

For the calculation of  $i$  the theoretical value  $1,855^\circ$  was chosen for the molecular depression in 1000 cc of water.

We then have  $i = \frac{t}{1,855 \cdot c'}$ , when  $t$  is the depression of the solidifying point.

The graphic representation, in which  $t$  is represented as function

$c'$	Depres- sion of S.p. $t$	$i = \frac{t}{1,855c'}$	$c'$	Depres- sion of S.p. $t$	$i = \frac{t}{1,855c'}$
<i>Sodium chloride.</i>			<i>Potassium chloride.</i>		
0.9539	3.180°	1.797	0.9486	3.201°	1.819
0.6224	2.095	1.814	0.7964	2.696	1.821
0.4011	1.361	1.829	0.6120	2.078	1.830
0.3772	1.283	1.833	0.5016	1.710	1.838
0.1702	0.586	1.857	0.3047	1.051	1.859
0.1501	0.518	1.861	0.1571	0.549	1.884
0.04014	0.142	1.91	0.07565	0.269	1.918
0.03042	0.109	1.93	0.02283	0.082	1.94
0.01161	0.042	1.95	0.01301	0.047	1.95
<i>Magnesium chloride.</i>			<i>Calcium chloride.</i>		
0.9583	6.063°	3.410	1.0092	5.966°	3.188
0.9795	4.726	3.185	0.8156	4.494	2.970
0.7078	4.033	3.072	0.6285	3.243	2.782
0.5322	2.847	2.883	0.4840	2.401	2.674
0.4889	2.577	2.841	0.3422	1.645	2.590
0.3852	1.972	2.759	0.2992	1.424	2.565
0.2280	1.146	2.710 <sup>1)</sup>	0.1968	0.933	2.556 <sup>1)</sup>
0.1917	0.964	2.711	0.1384	0.664	2.586
0.08023	0.408	2.741	0.07150	0.354	2.669
0.03135	0.163	2.80	0.03555	0.181	2.74
0.01352	0.074	2.95	0.01297	0.070	2.91
			0.00611	0.034	3.0

<sup>1)</sup> Minimum value of  $i$ .

of the concentration, yields for NaCl and KCl almost straight lines whereas those for MgCl<sub>2</sub> and CaCl<sub>2</sub> exhibit a slight bending upwards at the greater concentrations.

The values of  $i$  exhibit with MgCl<sub>2</sub> and CaCl<sub>2</sub> a minimum for  $c = \pm 0,2$ , whilst also here, contrary to the calculation from  $A$ , those of MgCl<sub>2</sub> are larger than those of CaCl<sub>2</sub>. Also the difference between NaCl and KCl is here smaller than followed from the  $A$  determinations.

The most trustworthy observations of other investigators mostly agree well with those of mine for KCl and NaCl, whereas those for MgCl<sub>2</sub> and CaCl<sub>2</sub> exhibit at both sides deviations of at most 2% of the value of  $t$  according to the graphic representation.

The determinations of the boiling points were carried out in metal vessels internally silver plated and surrounded by a steam jacket. In order to avoid corrections for the barometric pressure, a second vessel with pure water was always boiled under exactly the same conditions as the one containing the saline solution. An exchange of the thermometers in the two vessels could always take place without any danger of escape of vapour by placing these thermometers in a thin-walled tube containing mercury. These tubes were placed in the two vessels at an equal depth so that no correction for the hydrostatic pressure was required. By lengthening the refrigerating tube until it penetrates lower into the boiling vessel it was avoided that the colder reflux water had an influence on the thermometer bulb.

A retardation of boiling was counteracted by placing in each vessel 200 grams of clear glass beads and 10 silver tetrahedrons. A correction of the concentration for the water withdrawn from the solution by evaporation was applied. By experimenting this was determined as 0.2% of the concentration when the vessel contained 250 cc. of liquid. The concentration was determined before as well as after the boiling and then yielded no measurable differences. The necessary scale corrections were introduced on the thermometer. The calculation of  $c'$  from  $c$  was executed as directed above. Here also, these quantities relate to a temperature of 15°.

The graphic representation in which  $t$  was again plotted as function of  $c$  shows that the faintly bent curved lines for NaCl and KCl almost coincide, NaCl now being situated a little higher than KCl. Just as with the solidifying points, MgCl<sub>2</sub> is again higher than CaCl<sub>2</sub>.

In the calculation of  $i$  the theoretical value 0,52° was again chosen for the molecular increase of the boiling point in 1000 cc. of water. The values of  $i$  now exhibit with all salts a minimum, with NaCl and KCl for  $c' = \pm 0,3$  and with MgCl<sub>2</sub> and CaCl<sub>2</sub> for  $c' = \pm 0,2$ .

The results of other investigators exhibit in a graphic representation, also mutually, much stronger differences than with the depressions of the solidifying point. As a rule the values found by me are situated lower, probably in consequence of a retardation of boiling during measurements in glass apparatus according to BECKMANN. My observations show a good relative agreement with those of SMITS<sup>1)</sup>, although this observer, notwithstanding metal vessels, always found somewhat higher values. In part, these small differences are probably due to the correction of  $c'$  for the water evaporated, which SMITS does not seem to have applied. Here follow my results.

For the purpose of comparison of the results here obtained I have

$c'$	B.p. increase $t$	$i = \frac{t}{0.52 c'}$	$c'$	B.p. increase $t$	$i = \frac{t}{0.52 c'}$
<i>Sodium chloride.</i>			<i>Potassium chloride.</i>		
1.0342	0.950°	1.767	1.0263	0.932°	1.748
0.7729	0.694	1.726	0.7751	0.686	1.703
0.5147	0.454	1.697	0.5106	0.445	1.675
0.3532	0.310	1.688	0.3482	0.301	1.663 <sup>2)</sup>
0.2601	0.228	1.686 <sup>1)</sup>	0.2622	0.227	1.664
0.1721	0.153	1.710	0.1703	0.148	1.670
0.0962	0.089	1.78	0.1053	0.094	1.72
0.05128	0.049	1.84	0.05619	0.052	1.78
<i>Magnesium chloride.</i>			<i>Calcium chloride.</i>		
1.0151	1.633°	3.094	1.0052	1.562°	2.988
0.7698	1.116	2.785	0.7499	1.054	2.704
0.5146	0.672	2.510	0.5101	0.657	2.477
0.3551	0.435	2.356	0.3482	0.421	2.326
0.2558	0.304	2.282 <sup>1)</sup>	0.2528	0.298	2.264
0.1671	0.199	2.286	0.1712	0.202	2.270
0.0946	0.115	2.34	0.0972	0.117	2.32
0.04832	0.060	2.39	0.05183	0.064	2.37

<sup>1)</sup> Zs. phys. Chem. **39**, 385 (1901).

<sup>2)</sup> Minimum value of  $i$ .

C Gram mol. p. L. solution	$i$ from $\Delta$ at $0^\circ$	$i'$ at solidifying point	$i'-i$ at $0^\circ$	$i$ from $\Delta$ at $100^\circ$	$i'$ from boiling point	$i'-i$ at $100^\circ$
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*Sodium chloride*

1.000	1.719	1.795	0.076 ↑	1.609	1.764	0.155 ↑
0.750	1.742	1.807	0.065 ↑	1.642	1.725	0.083 ↑
0.500	1.766	1.821	0.055 ↑	1.674	1.697	0.023 ↑
0.250	1.806	1.846	0.040 ↑	1.724	1.687	-0.037 ↓
0.100	1.858	1.884	0.026 ↑	1.787	1.776	-0.011 ↓
0.050	1.892	1.905	0.013 ↑	1.831	1.840	0.009 ↓

*Potassium chloride*

1.000	1.777	1.816	0.039 ↑	1.670	1.748	0.078 ↑
0.750	1.793	1.823	0.030 ↑	1.695	1.702	0.007 ↑
0.500	1.809	1.837	0.028 ↑	1.720	1.674	-0.046 ↓
0.250	1.837	1.869	0.032 ↑	1.769	1.665	-0.104 ↓
0.100	1.871	1.906	0.035 ↑	1.826	1.723	-0.103 ↓
0.050	1.895	1.928	0.033 ↑	1.863	1.784	-0.079 ↓

*Magnesium chloride*

1.000	2.055	3.485	1.430 ↑	1.886	3.094	1.208 ↑
0.750	2.125	3.140	1.015 ↑	1.984	2.773	0.789 ↑
0.500	2.195	2.858	0.663 ↑	2.082	2.498	0.416 ↑
0.250	2.330	2.718	0.388 ↑	2.245	2.282	0.037 ↑
0.100	2.497	2.736	0.239 ↑	2.423	2.338	-0.085 ↓
0.050	2.620	2.780	0.160 ↑	2.546	2.390	-0.156 ↓

*Calcium chloride*

1.000	2.113	3.195	1.082 ↑	1.936	3.006	1.070 ↑
0.750	2.176	2.913	0.737 ↑	2.033	2.719	0.686 ↑
0.500	2.239	2.684	0.445 ↑	2.131	2.470	0.339 ↑
0.250	2.359	2.562	0.205 ↑	2.279	2.264	-0.015 ↓
0.100	2.504	2.632	0.128 ↑	2.452	2.318	-0.134 ↓
0.050	2.611	2.710	0.099 ↑	2.567	2.373	-0.194 ↓

represented  $i$  graphically from the solidifying and the boiling points as a function of  $c$ .

From this I have interpolated the values of  $i$  at the same concentrations as used in the determination of  $A$ . The third decimal of  $i'$  is, however, very vague on account of the powerful bends in the vicinity of the minima, which the thus obtained lines exhibit. From the differences of the dynamically obtained values of  $i'$  and those of  $i$  from  $A$  at corresponding temperatures we can control the previously mentioned views with a sufficient accuracy. From this appears the following.

At  $0^\circ$   $i'$  is always greater than  $i$  and the difference increases regularly with the concentration (with KCl we found small oscillations in the third decimal, so within experimental errors). With the most hydrated salt, namely  $\text{MgCl}_2$ , the increase of  $i' - i$  is the strongest, then follows  $\text{CaCl}_2$ , then  $\text{NaCl}$ , whilst the feeblest hydrated salt KCl shows the least increase of  $i' - i$ . With  $\text{MgCl}_2$  and  $\text{CaCl}_2$  the factor  $b$  seems to predominate in the large concentrations for there the decrease of  $i' - i$  with the dilution is much stronger than it is in the case of  $\text{NaCl}$ . Not in the case of a single salt does the factor  $a$  become so predominant that the influence of the hydration becomes also subdued. At  $100^\circ$ , on the other hand,  $i' - i$ , in the case of all salts, occasionally becomes negative, so that the influence of  $a$  is there stronger than that of  $b$  and the hydration together. With  $\text{NaCl}$  and KCl  $i' - i$  even exhibits a minimum, so that with these salts in the smallest concentrations the hydration seems to gain the best of  $a$ .

With  $\text{MgCl}_2$  and  $\text{CaCl}_2$  the differences at  $100^\circ$  are smaller than at  $0^\circ$  owing to the lesser hydration of these salts at a higher temperature. At the smallest concentrations the predominance of  $a$  steadily increases so that finally  $i' - i$  becomes fairly strongly negative.

As in the calculation of  $i$  the choice of  $A_\infty$  had to be rather arbitrary, whereas the molecular depression of the solidifying points and the rise of the boiling points could not be determined in a direct manner in consequence of the same perturbing influences that occurred in the solutions investigated, I cannot credit the results of  $i' - i$  with possessing absolute values. The direction in which  $i' - i$  changes with the concentration will, however, remain the same when another choice is made from the said constants. This direction and the velocity with which the change takes place can, however, just give us some insight into the strength of the influence of the perturbing causes, each separately. For a more detailed discussion on this point, I must again refer to the more elaborate article in the *Chemisch Weekblad* (1915).

Dec. 1914.

*Chem. Laboratory of the H.B.S. Bois le Duc.*

**Astronomy.** — “*On the figure of the planet Jupiter.*” By Prof. W. DE SITTER.

The potential function of a body possessing axial symmetry is <sup>1)</sup>

$$V = m \left[ \frac{1}{r} + \sum_1^{\infty} \frac{B_i}{r^{i+1}} P_i(\sin \sigma) \right],$$

where

$$B_i = \frac{1}{m} \int \rho^i P_i \left( \frac{\xi}{\rho} \right) dm.$$

In these formulas the axis of symmetry is chosen as axis of  $\xi$ . The coordinates of the element of mass  $dm$  are  $\xi, \eta, \zeta$ ;  $\rho^2 = \xi^2 + \eta^2 + \zeta^2$ , and the integrals must be extended over the whole body. Further  $\sigma$  is the planetocentric latitude, and  $P_i$  are the zonal harmonics of order  $i$ . If the origin of coordinates is taken in the centre of gravity, we have

$$B_1 = 0.$$

If the plane of  $\xi, \eta$  is a plane of symmetry, then also

$$B_3 = 0, \quad B_5 = 0, \dots \text{ etc.}$$

I adopt from the theory of the four large satellites

$$\frac{B_2}{b^2} = -0.01462.$$

The motion of the perijove of satellite V then gives

$$\frac{B_4}{b^4} = +0.00058.$$

By analogy we can conclude

$$\frac{B_6}{b^6} = -0.00002.$$

The effect of the term in  $B_6$  can thus never amount to more than a few units in the fifth decimal place, even at the surface of the planet. Since the values of  $B_2$  and  $B_4$  are uncertain to a larger amount than this, we neglect  $B_6$  altogether.

If now the body rotates about the axis of  $\zeta$  with the velocity  $\omega$ , we must, at the surface, have

$$V_0 = fm \left[ \frac{1}{r} + \frac{B_2}{r^3} P_2(\sin \sigma) + \frac{B_4}{r^5} P_4(\sin \sigma) \right] + \frac{1}{2} \omega^2 r^2 \cos^2 \sigma = \text{const.}$$

If we put

$$\varrho = \frac{\omega^2 b^3}{fm},$$

where  $b$  is the equatorial semidiameter, and

<sup>1)</sup> TISSERAND, *Méc. cél.* II p. 319—322.

$$\frac{fm}{V_0} = a,$$

then we find

$$\frac{r}{a} = 1 + \frac{B_2}{r^2} P_2(\sin \sigma) + \frac{B_4}{r^4} P_4(\sin \sigma) + \frac{1}{2} \varrho \frac{r^3}{b^3} \cos^2 \sigma. \quad (1)$$

The value of  $\omega$  is different for different latitudes. At the equator the period of rotation is nearly

$$T_0 = 9^{\text{h}}50^{\text{m}}.5.$$

In higher latitudes in the northern hemisphere it is about

$$T_1 = 9^{\text{h}}55^{\text{m}}.6$$

while in the southern hemisphere the average is

$$T_1' = 9^{\text{h}}55^{\text{m}}.2.$$

In the northern hemisphere  $T_1$  appears to increase somewhat from the equator to the pole, while in the southern hemisphere there seems to be a slight decrease<sup>1)</sup>. These results are, however, still rather uncertain and it seems better to adopt a mean value.

For  $T_0 = 9^{\text{h}}50^{\text{m}}.5$  we have  $\varrho_0 = 0.09047$

and for  $T_1 = 9^{\text{h}}55^{\text{m}}.5$  „ „ „  $\varrho_1 = 0.08971$

If now we write the equation (1) first for a point on the equator [ $r=b$ ], and then for the pole [ $r=b(1-\varepsilon_1)$ ], taking both times  $\varrho = \varrho_1$ , we find the following condition determining  $\varepsilon_1$

$$\frac{\varepsilon_1}{1-\varepsilon_1} - \frac{1}{2} \varrho_1 = -\frac{1}{2} \frac{B_2}{b^2} [1+2\lambda^3] + \frac{3}{8} \frac{B_4}{b^4} [1-\frac{8}{3}\lambda^5],$$

where

$$\lambda = \frac{1}{1-\varepsilon_1}.$$

I thus find

$$\varepsilon_1 = 0.06494 = 1/15.40$$

From the eclipses of the satellites observed at Harvard College I derived<sup>2)</sup>:

From satellite	I	$\varepsilon = 0.0604 \pm .0030$
„	„	II .0764 $\pm$ 15
„	„	III .0544 $\pm$ 30
„	„	IV .0649 $\pm$ 10

It is well known that also the values of  $\varepsilon$  derived by different observers from micrometrical measures of the diameters are very discordant. They range from about 0.055 to 0.075. The value derived

<sup>1)</sup> STANLEY WILLIAMS, Observatory 1913, page 465.

<sup>2)</sup> Monthly Notices LXXI. page 96.

here from the equation (1) is probably more exact than any of these.

This value of  $\varepsilon_1$  has been used for the computation of the values of the radiusvector given in the second, third and fourth columns of the following table. The third and fourth columns were computed by the equation (1), using for  $q$  the values  $q_0$  and  $q_1$  respectively.

The table gives  $\frac{r}{b} - 1$ .

$\delta$	Ellipsoid	Equipotential surface		Difference		Diff. in km.
		$q_0$	$q_1$	$q_0$	$q_1$	
0°	0.00000	+ 0.00042		+ 0.00042		+ 30
5	— .00055	— .00014	— 0.00056	+ 40	— 0.00001	+ 28
10	— .00216	— .00181	— .00222	+ 35	— 6	0
15	— .00478	— .00452	— .00490	+ 26	— 12	— 8
20	— .00830		— .00850		— 20	— 14
30	— .01750		— .01786		— 36	— 26
40	— .02843		— .02890		— 47	— 34
50	— .03968		— .04014		— 46	— 33
60	— .04990		— .05026		— 36	— 26
70	— .05799		— .05819		— 20	— 14
80	— .06317		— .06322		— 6	— 4
90	— .06494		— .06494		0	0

The deviation from the ellipsoid thus consists of a protuberance along the equator, produced by the increase of the velocity of rotation, and a depression in mean latitudes<sup>1)</sup>. The transition probably takes place rather suddenly somewhere near the latitude 7°.

We have up to now taken no account of the variability of  $\omega$  in

<sup>1)</sup> If quantities of the order of  $\varepsilon^3$  are neglected, the deviation from the ellipsoid is easily shown to be (for constant  $\omega$ ) of the form

$$- \kappa \sin^2 2\delta,$$

where

$$\kappa = \frac{5}{8} \varepsilon Q - \frac{7}{8} \varepsilon^2 + \frac{35}{32} \frac{B_4}{b^4} = 0.00058.$$

The actual depression is only about  $\frac{1}{5}$  of this.

For the earth the value of  $\kappa$  is of the order of 0.0000005 = 3 meters.

the higher latitudes. A difference of  $0^m.4$  in  $T$  corresponds to a difference of  $0.00006$  in  $\frac{1}{2} \varrho$ . Therefore, if we had used for each latitude its own value of  $\omega$  or  $\varrho$ , only the last decimal of  $r/b$  would have been affected. In that case, however, we must also dismiss the assumption  $B_3 = 0$ . Of the true value of  $B_3$  we know nothing, but we can assert with considerable certainty that it will be of the same order of magnitude as the difference between the northern and southern rotations, i. e. that it will, like the other causes of uncertainty discussed above, not exceed the fifth decimal place.

The deviations from the ellipsoid are, of course, far beyond the reach of direct micrometrical measures. In fact they are always below  $0''.01$ . The effect on the times of the phenomena of the satellites is, at latitude  $60^\circ$ ,  $0^s.034$  for satellite I and  $0^s.070$  for satellite IV, which also is beyond the accuracy of the observations. Thus for all practical purposes we can treat the surface of Jupiter as a true ellipsoid.

**Chemistry.** — “*The Allotropy of Cadmium V*”. By Prof. ERNST COHEN and W. D. HELDERMAN.

*The heat of Transformation in the reaction  $Cd(\alpha) \rightleftharpoons Cd(\gamma)$ .*

1. As we pointed out some time ago in our sixth communication on the thermodynamics of standard cells,<sup>1)</sup> in calculating the chemical energy of the WESTON cell we have to take into account that cadmium is able to exist in different allotropic modifications. While this problem will be treated later in full, it may be pointed out here that it is very important to know the quantity of heat which is involved in the reaction



The investigations to be described here have reference to this problem.

2. Up to the present such a heat of transformation of a metal has only been determined in one single case. Some months ago BRÖNSTED<sup>2)</sup> carried out some measurements on the heat of the transformation

grey tin  $\rightarrow$  white tin.

<sup>1)</sup> Chem. Weekblad **11**, 740 (1914).

<sup>2)</sup> Zeitschr. f. physik. Chemie **88**, 479 (1914).

He found it to be 532 gram calories per gram atom of tin at 0° C.

3. For several reasons the calorimetric method used by BRÖNSTED cannot be applied to our case. We therefore carried out our experiments with a *Transition Cell* of the sixth kind, which has been described by ERNST COHEN.<sup>1)</sup>

This cell is constructed according to the scheme:

Electrode of a metal M in its <i>stable</i> modification.	Solution of a salt of M of an arbitrary concentration.	Electrode of the metal M in its <i>metastable</i> modification.
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4. Hitherto it was impossible to make a quantitative application of this cell, as no metal, having a transition point, was known which exists in an electrically sharply defined condition.

Our measurements will prove that the transformation  $\alpha$ -cadmium  $\rightleftharpoons$   $\gamma$ -cadmium is especially suitable for such an investigation.

As we have in view the carrying out of some other measurements with our  $\alpha$ - and  $\gamma$ -cadmium, we have not brought them together in one single transition cell, but used them as the negative electrodes in cells which were constructed according to the scheme given by HULETT. These cells were studied separately. Consequently our cells were made up as follows:

Cd- $\alpha$	Unsaturated solution of CdSO <sub>4</sub> of an arbitrary concentration	Cadmium amalgam...!( $\alpha$ -cell). 8 percent by weight
and		
Cd- $\gamma$	Unsaturated solution of CdSO <sub>4</sub> of an arbitrary concentration	Cadmium amalgam... ( $\gamma$ -cell). 8 percent by weight.

5. On applying the equation of GIBBS—VON HELMHOLTZ:

$$E_e = \frac{E_c}{n\epsilon} + T \frac{dE_c}{dT}$$

to the  $\alpha$ - and  $\gamma$ -cell separately, we find:

$$(E_e)_\alpha = \frac{(E_c)_\alpha}{n\epsilon} + T \left( \frac{dE_c}{dT} \right)_\alpha \dots \dots \dots (\alpha\text{-cell})$$

and:

$$(E_e)_\gamma = \frac{(E_c)_\gamma}{n\epsilon} + T \left( \frac{dE_c}{dT} \right)_\gamma \dots \dots \dots (\gamma\text{-cell})$$

<sup>1)</sup> Zeitschr. f. physik. Chemie 30, 623 (1899)

$(E_e)_\alpha$  represents the electric energy of the  $\alpha$ -cell at  $T^\circ$ ;  $(E_c)_\alpha$  the quantity of heat which is generated if at  $T^\circ$  one gram atom of  $\alpha$ -Cadmium is dissolved in an unlimited quantity of cadmium amalgam (8 percent by weight).

The signification of  $(E_e)_\gamma$  and  $(E_c)_\gamma$  is quite analogous.

6. From our equations we get:

$$(E_c)_\gamma - (E_c)_\alpha = n\varepsilon \left[ (E_e)_\gamma - (E_e)_\alpha - T \left\{ \left( \frac{dE_e}{dT} \right)_\gamma - \left( \frac{dE_e}{dT} \right)_\alpha \right\} \right]. \quad (1)$$

The expression on the left represents the heat of transformation which accompanies the change of 1 gram atom  $\gamma$ -cadmium into  $\alpha$ -cadmium, i. e. the value to be determined.

Therefore we have only to measure the E.M.F. as well as the temperature coefficients of the  $\alpha$ - and  $\gamma$ -cell at  $T^\circ$ .

7. As we pointed out some time ago the cells which have been studied by HULETT <sup>1)</sup> are our  $\gamma$ -cells. From his determinations between  $0^\circ$  and  $40^\circ$  C. it follows that

$$(E_e)_\gamma^{t^\circ} = 0.05047 - 0.0002437 (t - 25) \text{ Volt} \dots \dots (2)$$

8. We constructed our  $\alpha$ -cells starting from  $\gamma$ -cells, in which the  $\gamma$ -cadmium was transformed into  $\alpha$ -cadmium.

The way in which these  $\gamma$ -cells were prepared and in which their E. M. F. was determined has been described in full in our third paper on the allotropy of cadmium. <sup>2)</sup> As standard cells we used two WESTON-cells and two CLARK-cells which were standing in a thermostat at  $25.0^\circ$ . The E. M. F. of the WESTON-cell was assumed to be 1.0181 Volt at  $25.0^\circ$ .

The ratio  $\left( \frac{\text{E. M. F. CLARK}}{\text{E. M. F. WESTON}} \right)_{25.0^\circ}$  was found to be:

Oct. 31. 1914 1.3948

Dec. 17. 1914 1.3947

Jan. 19. 1915 1.3947

We prepared 11  $\gamma$ -cells. At  $25.0^\circ$  their E. M. F. was 0.0504 Volt. After standing for a fortnight at  $25.0^\circ$  the  $\gamma$ -cadmium was transformed into the  $\beta$ -modification as was shown by the fact that the E. M. F. had decreased to 0.048 Volt at  $25.0^\circ$ . In order to transform the  $\beta$ -modification into  $\alpha$ -cadmium we put the cells for a fortnight into a thermostat which was kept at  $47.5^\circ$  C. We now

<sup>1)</sup> Trans. Americ. electrochem. Soc. **15**, 435 (1909). HULETT used a 10 percent amalgam (by weight). This is a two-phase system between  $0^\circ$  and  $40^\circ$ .

<sup>2)</sup> These Proc. Vol. XVII. p. 122.

put a fresh amalgam into the cells, while a fresh solution of cadmium sulphate was also introduced. We found that in 4 cells (out of eleven) the  $\beta$ -cadmium had been transformed into the  $\alpha$ -modification. The E. M. F. of these cells was 0.0474 Volt at 25°0. (See our third paper on the allotropy of cadmium).

9. These  $\alpha$ -cells were systematically investigated at 25°0, 20°0 and 15°0 respectively, in order to determine their temperature coefficients. Table I contains the results.

The measurements may be represented by the equation:

$$(E_e)_{\alpha}^{t^{\circ}} = 0,04742 - 0,000200 (t - 25) \text{ Volt. . . . . (3)}$$

TABLE I.  
E. M. F. of  $\alpha$ -Cells (Volt).

Date	Temperature	Cell H <sub>2</sub>	Cell H <sub>4</sub>	Cell H <sub>5</sub>	Cell H <sub>6</sub>	Mean
Jan. 14	25.0°	0.04751	0.04740	0.04763	0.04758	0.04742
15 a.m.	25.0	0.04725	0.04797	0.04710	0.04714	
15 p.m.	25.0	0.04721	0.04790	0.04710	0.04710	
16	25.0	0.04728	0.04794	0.04731	0.04731	
Jan. 18	20.0°	0.04848	0.04837	—	—	0.04841
19 a.m.	20.0	0.04843	0.04833	—	—	
19 p.m.	20.0	0.04849	0.04841	—	—	
19 night	20.0	0.04832	0.04836	—	—	
20	20.0	0.04840	—	—	—	
21	20.0	0.04843	—	0.04850	0.04860	
22	20.0	0.04833	—	0.04833	0.04843	
Jan. 23 am.	15.0°	0.04908	—	0.04944	0.04947	0.04943
23 pm.	15.0	0.04925	—	0.04966	0.04968	
24	15.0	0.04959	—	0.04948	0.04956	
25	15.0	0.04924	—	0.04928	0.04937	
Jan. 25	25.0°	0.04752	—	0.04759	0.04761	

10. The reproducibility of these cells is not less good than that of the  $\gamma$ -cells. Calculating from (3) the E. M. F. of an  $\alpha$ -cell at  $0^\circ$  C. the value  $(E_e)_\alpha^{0^\circ} = 0.05245$  Volt is found, while a cell which had formerly been measured at  $0^\circ$  C. (see our third paper on the allotropy of cadmium) gave the value 0,05225 Volt. This cell had been prepared at a different time using different materials.

11. In order to calculate the heat of transformation of  $\alpha$ -cadmium into  $\gamma$ -cadmium at  $18^\circ.0$  C. we have to introduce the numerical values into our equation (1).

From (2) we find:

$$(E_e)_\gamma^{18^\circ} = 0,05217 \text{ Volt.}$$

$$\left(\frac{dE_e}{dT}\right)_\gamma^{18^\circ} = -0,0002437 \frac{\text{Volt}}{\text{degree}}.$$

From (3) we get:

$$(E_e)_\alpha^{18^\circ} = 0,04885 \text{ Volt.}$$

$$\left(\frac{dE_e}{dT}\right)_\alpha^{18^\circ} = -0,000200 \frac{\text{Volt}}{\text{degree}}$$

$$(E_c)_\gamma^{18^\circ} - (E_c)_\alpha^{18^\circ} = [0,05217 - 0,04885 - 291 (-0,0002437 + \\ + 0,000200)] 46105 = \mathbf{739} \text{ gram calories.}$$

If one gram atom of  $\alpha$ -cadmium is transformed into  $\gamma$ -cadmium, the change is accompanied at  $18^\circ.0$  C. by an absorption of 739 gram calories.

12. It may be pointed out that the temperature at which  $(E_c)_\alpha = (E_c)_\gamma$  represents the *metastable* transition point of the reaction  $\alpha$ -cadmium  $\rightleftharpoons$   $\gamma$ -cadmium.

If we put (2) = (3), we find:

$$0.00305 = 0.0000437 (t - 25) \\ t = 94^\circ,8$$

Utrecht, January 1915.

VAN 'T HOFF-Laboratory.

**Chemistry.** — Note on our paper: “*The Allotropy of Lead I*”  
by Prof. ERNST COHEN and W. D. HELDERMAN.

In our first communication on the Allotropy of Lead <sup>1)</sup> we stated that we resumed our investigations on this subject after having received a letter from Mr. HANS HELLER in Leipsic which showed us the way in which fresh experiments had to be directed. In this letter Mr. HELLER kindly invited us to continue these investigations.

As Mr. HELLER writes in a letter dated Jan. 21<sup>st</sup> 1915: “Gewünscht hätte ich freilich, dass der Ort, an dem ich meine Versuche machte, das hiesige Chemische Laboratorium, in der Veröffentlichung genannt worden wäre”, we comply with pleasure with his request by publishing the above statement.

Utrecht, January 1915.

VAN 'T HOFF-Laboratory.

**Mathematics.** — “*Characteristic numbers for a triply infinite system of algebraic plane curves*” By Prof. JAN DE VRIES.

(Communicated in the meeting of Dec. 30, 1914).

1. The curves of order  $n$ ,  $c^n$ , of a triply infinite system  $\Gamma$  (complex) cut a straight line  $l$  in the groups of an involution  $I_n^3$  of the third rank. The latter possesses  $4(n-3)$  groups with a quadruple element;  $l$  is consequently four-point tangent,  $t_4$ , for  $4(n-3)$  curves  $c^n$ . Any point  $P$  is base-point of a net  $N$  belonging to  $\Gamma$ , hence point of undulation,  $R_4$ , for six curves  $c^n$ . <sup>2)</sup> If  $l$  rotates round  $P$ , the points  $R_4$  describe a curve  $(R_4)_P$  of order  $(4n-6)$ , with sixfold point  $P$ .

The tangent  $t_4$  cuts  $c^n$  moreover in  $(n-4)$  points  $S$ ; the locus  $(S)_P$  has apart from  $P$ ,  $4(n-3)(n-4)$  points in common with  $l$ . The tangents  $t_4$  of a net envelop a curve of class  $6n(n-3)$  <sup>3)</sup>; as  $P$  is sixfold point on the curve  $(R_4)$  belonging to the net determined by  $P$ ,  $P$  will lie on  $6n(n-3) - 24$  or  $6(n-4)(n+1)$  tangents  $t_4$ , of which the point of contact  $R_4$  lies outside  $P$ . So  $P$  is a  $6(n-4)(n+1)$ -fold point on  $(S)_P$ , and the order of this curve is  $4(n-3)(n-4) + 6(n+1)(n-4)$  or  $2(n-4)(5n-3)$ .

Let us now consider the correspondence which is determined in

<sup>1)</sup> Proceedings 17, 822 (1914).

<sup>2)</sup> Cf. p. 937 of my paper: “*Characteristic numbers for nets of algebraic curves*”. (Proceedings Vol. XVII, p. 935). For the sake of brevity this paper will be quoted by N.

<sup>3)</sup> N. p. 936.

a pencil of rays with vertex  $M$  by the pairs of associated points  $R_4$  and  $S$ . Any ray  $MR_4$  contains  $(4n-6)$  points  $R_4$ , consequently determines  $(4n-6)(n-4)$  points  $S$ ; any ray  $MS$  contains  $(n-4)(10n-6)$  points  $S$ , produces therefore as many rays  $MR_4$ . To the  $(n-4)(14n-12)$  coincidences, the ray  $MP$  belongs  $4(n-3)(n-4)$  times; for on  $MP$  lie  $4(n-3)$  points  $R_4$ , hence  $4(n-3)(n-4)$  points  $S$ . The remaining coincidences arise from the coinciding of a point  $R_4$  with one of the corresponding points  $S$ . This takes place in the point of contact  $R_5$  of a  $c^n$  with a five-point tangent  $t_5$ . From this it ensues that the five-point tangents of  $\Gamma$  envelop a curve of class  $10n(n-4)$ .

We further consider the symmetrical correspondence between the rays of  $(M)$ , containing two intersections  $S, S'$  belonging to the same point of contact  $R_4$ . Its characteristic number is apparently  $(10n-6)(n-4)(n-5)$ . On  $MP$  lie  $4(n-3)(n-4)(n-5)$  pairs  $S, S'$ ; as many coincidences are represented by  $MP$ . The remaining coincidences arise from the coinciding of a point  $S'$  with a point  $S$ , hence arise from lines  $t_{4,2}$ , which have with a  $c^n$  in a point  $R_4$  a four-point contact, and in a point  $R_2$  a two-point contact. *The tangents  $t_{4,2}$  envelop therefore a curve of class  $16n(n-4)(n-5)$ .*

2. Any point of the arbitrary straight line  $a$  is, as basepoint of a net belonging to  $\Gamma$ , point of contact  $R_4$  for six curves  $c^n$ . The sextuples in this way coupled to  $a$  form a system  $[c^n]$ , of which the index is equal to the order of the locus of the points of undulation  $R_4$  on the curves of the net set apart out of  $\Gamma$  by an arbitrary point  $P$ , consequently equal to  $3(6n-11)^1$ . The tangents  $t_4$ , of which the points of contact  $R_4$  lie on  $a$ , form a system  $[t_4]$  with index  $(4n-6)$  for through  $P$  pass  $(4n-6)$  straight lines  $t_4$ , having their point of contact  $R_4$  on  $a$  (§ 1). Two projective systems  $[c^r]$  and  $[c^s]$  with indices  $\rho$  and  $\sigma$  produce a curve of order  $(r\sigma + \rho s)$ . If to each  $c^n$  of the above system the line  $t_4$  is associated, which touches it on  $a$ , a figure arises of order  $3(6n-11) + n(4n-6)$ . The latter consists of the straight line  $a$  counted 24 times, and the locus of the points  $S$ , which each  $t_4$  has moreover in common with the corresponding  $c^n$ . This curve  $(S)_a$  is therefore of order  $(4n^2 + 12n - 57)$ .

For  $n = 4$ ,  $(S)_a$  is therefore of order 55. In a complex of curves  $c^4$  occur therefore 55 figures consisting of a  $c^3$  and a straight line  $c^1$ . If all  $c^4$  pass through 11 fixed points the straight lines  $c^1$  are apparently the sides of the complete polygon determined by the base-points.

To the intersections of  $(S)_a$  with  $a$  belong the  $4(n-3)$  groups of

<sup>1)</sup> N bl. 937.

$(n-4)$  points  $S$  arising from the  $c^n$  having  $a$  as tangent  $t_4$ . In each of the remaining intersections a point  $R_4$  has coincided with a point  $S$  into a point  $R_5$ . The points, where a  $c^n$  possesses a five-point tangent, lie therefore on a curve  $(R_5)$  of order  $(40n-105)$ .

For  $n=4$ , the number 55 is duly found.

**3.** To each  $c^n$  possessing a tangent  $t_5$ , we associate that tangent; the latter cuts it moreover in  $(n-5)$  points  $V$ . The locus of the points  $V$ , together with the curve  $(R_5)$  to be counted five times, is produced by the projective systems  $[c^n]$  and  $[t_5]$ . The system  $[t_5]$  has (§ 1) as index  $10n(n-4)$ . The curves  $c^n$  passing through a point  $P$  form a net; in this net occur  $15(n-4)(4n-5)$  curves with a  $t_5$ <sup>1)</sup>; this number is the index of  $[c^n]$ . For the order of the curve  $(V)$  is found  $15(n-4)(4n-5) + 10n^2(n-4) - 5(40n-105) = 5(n-5)(2n^2 + 14n - 33)$ .

In the pencil of rays  $(M)$  the pairs of points  $R_5, V$  determine a correspondence with characteristic numbers  $(n-5)(40n-105)$  and  $(n-5)(10n^2 + 70n - 165)$ . The  $10n(n-4)$  tangents  $t_5$  passing through  $M$  produce each  $(n-5)$  coincidences. As the remaining ones arise from the coinciding of  $R_5$  with  $V$ , it appears that  $\Gamma$  contains  $30(n-5)(5n-9)$  curves with a six-point tangent  $t_6$ .

The symmetrical correspondence  $(MV, MV')$  has as characteristic number  $(10n^2 + 70n - 165)(n-5)(n-6)$ , while the  $10n(n-4)$  tangents  $t_5$  passing through  $M$  represent each  $(n-5)(n-6)$  coincidences. From this ensues that  $\Gamma$  possesses  $10(n-5)(n-6)(n^2 + 18n - 33)$  curves with a tangent  $t_{5,2}$ .

**4.** The  $I_n^3$ , which  $\Gamma$  determines on  $l$ , possesses  $6(n-3)(n-4)$  groups in which a triple element occurs beside a twofold one; consequently is  $l$  for  $6(n-3)(n-4)$  curves a tangent  $t_{2,3}$ . If  $l$  rotates round  $P$ , the points of contact  $R_2$  and  $R_3$  describe two curves  $(R_2)_{2,3}$  and  $(R_3)_{2,3}$ .  $P$  is as base-point of a net, point of contact  $R_2$  for  $3(n-4)(n+3)^2$ , point of contact  $R_3$  for  $(n-4)(n+9)^3$  curves. So  $(R_2)_{2,3}$  is of order  $(n-4)(3n+9) + 6(n-3)(n-4)$  or  $(n-4)(9n-9)$  and  $(R_3)_{2,3}$  of order  $(n-4)(n+9) + 6(n-3)(n-4)$  or  $(n-4)(7n-9)$ .

From the correspondence  $(MR_2, MR_3)$  may be deduced again that  $t_5$  envelops a curve of class  $10n(n-4)$ . (See § 1).

Each tangent  $t_{2,3}$  passing through  $P$  cuts the corresponding  $c^n$  in  $(n-5)$  points  $W$ ; on a ray passing through  $P$  lie therefore  $6(n-3)$

<sup>1)</sup> N p. 938.

<sup>2)</sup> N p. 943.

<sup>3)</sup> N p. 942.

$(n-4)(n-5)$  points of the curve  $(W)_P$ . The  $c^n$  passing through  $P$  form a net, of which the tangents  $t_{2,3}$  envelop a curve of class  $9n(n-3)(n-4)$ .<sup>1)</sup>

As  $P$  is point of contact  $R_2$  for  $(n-4)(3n+9)$  and point of contact  $R_3$  for  $(n-4)(n+9)$  curves of the net,  $P$  lies, as point  $W$ , on  $9n(n-3)(n-4) - 2(n-4)(3n+9) - 3(n-4)(n+9) = 9(n-4)(n-5)(n+1)$  tangents  $t_{2,3}$ . The order of  $(W)_P$  amounts therefore to  $6(n-3)(n-4)(n-5) + 9(n-4)(n-5)(n+1)$  or  $3(n-4)(n-5)(5n-3)$ .

Starting from the correspondence  $(R_3, W)$  we arrive again at the class of the curve enveloped by  $t_{4,2}$  (§ 1).

A new result is produced by the correspondence of the rays  $MR_2, MW$ . Its characteristic numbers are  $(9n-9)(n-4)(n-5)$  and  $(15n-9)(n-4)(n-5)$ . The ray  $MP$  represents  $6(n-3)(n-4)(n-5)$  coincidences. The remaining  $18n(n-4)(n-5)$  arise from coincidences  $R_2 \equiv W$ , consequently from tangents  $t_{3,3}$ . As each  $t_{3,3}$  determines two coincidences, *the twice osculating tangents  $t_{3,3}$  envelop a curve of class  $9n(n-4)(n-5)$ .*

The symmetrical correspondence between the rays connecting  $M$  with the pairs of points  $W, W'$ , belonging to the same  $c^n$ , has as characteristic number  $(n-4)(n-5)(n-6)(15n-9)$ . As  $MP$  represents  $6(n-3)(n-4)(n-5)(n-6)$  coincidences, and the remaining ones arise in pairs from tangents  $t_{2,2,3}$ , *the tangents  $t_{2,2,3}$  envelop a curve of class  $12n(n-4)(n-5)(n-6)$ .*

5. The  $I_n^3$ , which  $P$  determines on  $l$ , contains  $\frac{4}{3}(n-3)(n-4)(n-5)$  groups with three double elements; as many curves  $c^n$  have  $l$  as triple tangent  $t_{2,2,2}$ . In the net determined by  $P$  occur  $2(n+3)(n-4)(n-5)c^n$ , on which  $P$  is point of contact of a triple tangent.<sup>2)</sup> If  $l$  rotates round  $P$ , the points of contact describe therefore a curve of order  $4(n-3)(n-4)(n-5) + 2(n+3)(n-4)(n-5)$  or  $6(n-4)(n-5)(n-1)$ .

We further determine the order of the locus of the groups of  $(n-6)$  points  $Q$ , which  $l$  has moreover in common with the  $c^n$ , which it touches three times. The  $t_{2,2,2}$  belonging to the net with base-point  $P$  envelop a curve of class  $2n(n-3)(n-4)(n-5)$ .<sup>3)</sup> As  $P$  is point of contact for  $2(n+3)(n-4)(n-5)c^n$ , the number of  $c^n$  intersecting their  $t_{2,2,2}$  in  $P$  amounts to  $2n(n-3)(n-4)(n-5) - 4(n+3)(n-4)(n-5)$  or  $2(n+1)(n-4)(n-5)(n-6)$ . The order

<sup>1)</sup> N. p. 936.

<sup>2)</sup> N. p. 943.

<sup>3)</sup> N. p. 939.

of  $(Q)$  is therefore equal to  $2(n+1)(n-4)(n-5)(n-6) + \frac{1}{3}(n-3)(n-4)(n-5)(n-6)$  or  $\frac{2}{3}(5n-3)(n-4)(n-5)(n-6)$ .

The correspondence  $(MR, MQ)$  produces again the class of the envelop of  $t_{2,2,3}$  (§ 4).

From the symmetrical correspondence  $(MQ, MQ')$ , which has as characteristic number  $\frac{2}{3}(5n-3)(n-4)(n-5)(n-6)(n-7)$  and has in  $MP$   $\frac{1}{3}(n-3)(n-4)(n-5)(n-6)(n-7)$  coincidences, we find that the *quadruple tangents  $t_{2,2,2}$  envelop a curve of class  $\frac{1}{3}n(n-4)(n-5)(n-6)(n-7)$ .*

**6.** Any point of the arbitrary straight line  $a$ , is, as base-point of a net, point of contact  $R_3$  of  $(n-4)(n+9)$  tangents  $t_{2,3}$ .<sup>1)</sup> The locus  $(R_2)_a$  of the corresponding points of contact  $R_2$  has two groups of points in common with  $a$ ; the first group contains the  $(40n-105)$  intersections with the curve  $(R_3)$ , the second contains the  $6(n-3)(n-4)$  points  $R_2$ , where  $a$  is touched by the curves  $c^n$ , osculating it in a point  $R_3$ . From this ensues that  $(R_2)_a$  is of order  $(6n^2-2n-33)$ .

In order to find the order of the locus of the points  $W$ , which each  $t_{2,3}$  has in common with its  $c^n$ , we consider the figure produced by projective association of the corresponding systems  $[c^n]$  and  $[t_{2,3}]$ . The curves  $c^n$ , of the net determined by  $P$ , which possess a  $t_{2,3}$ , have their points of contact  $R_3$  on a curve of order  $3(n-4)(n^2+6n-13)^2$ ; the latter intersects  $a$  in the points  $R_3$  of the curves of  $[c^n]$  passing through  $P$ . The index of  $[t_{2,3}]$  is, see § 4,  $(n-4)(7n-9)$ . Considering that the figure produced is composed of  $3(n-4)(n+9)$  times the straight line  $a$ , twice the curve  $(R_2)_a$  and the locus  $(W)_a$ , we find for the order of the last-mentioned curve

$$(n-4)(3n^2+18n-39) + n(n-4)(7n-9) - 3(n-4)(n+9) - 2(6n^2-2n-33) = (n-5)(10n^2+4n-66).$$

The curve  $(W)_a$  cuts  $a$  in  $6(n-3)(n-4)$  groups of  $(n-5)$  points  $W$ ; in each of the remaining intersections a  $c^n$  has a four-point contact with a line  $t_{4,2}$ . *Consequently the points of contact  $R_4$  of the tangents  $t_{4,2}$  lie on a curve of order  $(n-5)(4n^2+46n-138)$ .*

The pairs of points  $R_2, W$  determine in a pencil of rays  $(M)$  a correspondence with characteristic numbers  $(n-5)(10n^2+4n-66)$  and  $(n-5)(6n^2-2n-33)$ . The  $(n-4)(7n-9)$  rays  $t_{2,3}$  passing through  $M$ , which have their point of contact  $R_3$  on  $a$ , represent each  $(n-5)$  coincidences. From this ensues that *the points of contact (inflectional points) of the twice osculating lines are situated on a curve of order  $(n-5)(9n^2+39n-135)$ .*

<sup>1)</sup> N. p. 942.

<sup>2)</sup> N. p. 940.

The symmetrical correspondence  $(MW, MW')$  has as characteristic number  $(n-5)(n-6)(10n^2+4n-66)$  and possesses  $(n-5)(n-6)$  coincidences in each of the  $(n-4)(7n-9)$  rays  $MR_3$ . The remaining ones arise in pairs from tangents  $t_{2,2,3}$ . So we find that *the inflectional points  $R_3$  of the tangents  $t_{2,2,3}$  lie on a curve of order  $\frac{1}{2}(n-5)(n-6)(13n^2+45n-168)$ .*

7. Let us now consider the system  $[c^n]$  of the curves which have the point of contact  $R_2$  of their tangent  $t_{2,3}$  on the straight line  $a$ . The curve  $(R_3)_a$  cuts  $a$  in  $(40n-105)$  points  $R_5$  and in  $6(n-3)(n-4)$  points  $R_3$ , where  $a$  osculates a  $c^n$ , for which it is tangent  $t_{2,3}$ . Consequently  $(R_3)_a$  is of order  $(6n^2-2n-33)$ .

The system  $[c^n]$  has as index  $(n-4)(6n^2+15n-36)^1$ ; for  $[t_{2,3}]$  the index is, see § 4,  $(n-4)(9n-9)$ . The figure produced by these projective systems consists of  $2(n-4)(3n+9)$  times the straight line  $a$ , three times the curve  $(R_3)_a$  and the locus of the points  $W^*$ , which each  $t_{2,3}$  has moreover in common with its  $c^n$ . For the order of  $(W^*)_a$  we find  $(n-4)(6n^2+15n-36) + n(n-4)(9n-9) - 2(n-4)(3n+9) - 3(6n^2-2n-33)$  or  $(n-5)(15n^2-3n-63)$ .

The number of the intersections of  $(W^*)_a$  with  $a$  again produces the order of the curve  $(R_3)_{3,3}$ .

The correspondence  $(MR_3, MW^*)$  has as characteristic numbers  $(n-5)(15n^2-3n-63)$  and  $(n-5)(6n^2-2n-33)$ , while each of the rays  $t_{2,3}$  passing through  $M$  represents  $(n-5)$  coincidences. From  $(n-5)[(15n^2-3n-63) + (6n^2-2n-33) - (n-4)(9n-9)]$  we find now that *the points of contact  $R_2$  of the tangents  $t_{2,4}$  are situated on a curve of order  $(n-5)(12n^2+40n-132)$ .*

The symmetrical correspondence  $(MW_1^*, MW_2^*)$  furnishes in the same way from  $(n-5)(n-6)[(30n^2-6n-126) - (n-4)(9n-9)]$  the result, that *the points of contact  $R_2$  of the tangents  $t_{2,2,3}$  lie on a curve of order  $(n-5)(n-6)(21n^2+39n-162)$ .*

8. Let us now consider the system  $[c^n]$  of the curves with triple tangent of which one of the points of contact,  $R_2$ , lies on the straight line  $a$ . The other two points of contact  $T_2$ , lie on a curve  $(T_2)_a$ , which has two groups of points in common with  $a$ . The former contains the  $(n-5)(4n^2+46n-138)$  points  $R_4$  of tangents  $t_{4,2}$  (§ 6), the latter the groups of three points of contact  $T_2$  lying on the curves  $c^n$ , for which  $a$  is triple tangent; these points are apparently to be counted twice. Consequently  $(T_2)_a$  is of order  $(n-5)(4n^2+46n-138) + 8(n-5)(n-4)(n-3)$  or  $(n-5)(12n^2-10n-42)$ .

<sup>1</sup>) N. p. 940.

We now consider again the figure produced by the projective systems  $[c^n]$  and  $[t_{2,2,2}]$ . The former has as index  $\frac{3}{2}(n-4)(n-5)(3n^2+5n-14)$ <sup>1)</sup>, the latter, see § 5,  $6(n-4)(n-5)(n-1)$ . As the figure produced consists of  $4(n+3)(n-4)(n-5)$  times the line  $a$ <sup>2)</sup>, twice the curve  $(T_2)_a$  and the locus of the points  $Q$ , which each  $c^n$  has moreover in common with its  $t_{2,2,2}$ , we find for the order of  $(Q)_a$   $\frac{3}{2}(n-4)(n-5)(3n^2+5n-14)+6(n-4)(n-5)(n-1)n-4(n-4)(n-5)(n+3)-2(n-5)(12n^2-10n-42)$  or  $\frac{1}{2}(n-5)(n-6)(21n^2-11n-72)$ .

The curve  $(Q)_a$  is cut by  $a$  in  $\frac{1}{3}(n-3)(n-4)(n-5)$  groups of  $(n-6)$  points  $Q$ , which are each to be counted thrice, and in a number of points  $(T_3)$ , where a  $c^n$  is osculated by a tangent  $t_{3,2,2}$ . From  $\frac{1}{2}(n-5)(n-6)(21n^2-11n-72)-4(n-3)(n-4)(n-5)(n-6)$  ensues again (§ 6), that *the points of contact  $T_3$  of the tangents  $t_{3,2,2}$  are situated on a curve of order  $\frac{1}{2}(n-5)(n-6)(13n^2+45n-168)$ .*

The correspondence between the points  $T_2$ , outside  $a$ , and the corresponding points  $Q$ , produces again the order of the curve  $(R_2)$  belonging to the tangents  $t_{2,2,3}$  (§ 7).

The symmetrical correspondence  $(MQ, MQ')$  has as characteristic number  $\frac{1}{2}(n-5)(n-6)(n-7)(21n^2-11n-72)$  and in each  $t_{2,2,2}$  passing through  $M(n-6)(n-7)$  coincidences. From  $(n-5)(n-6)(n-7)[(21n^2-11n-72)-6(n-1)(n-4)]$  ensues that *the locus of the points of contact of the quadruple tangents is a curve of order  $\frac{1}{3}(n-5)(n-6)(n-7)(15n^2+19n-96)$ .*

**9.** Let us now consider the figure determined by the projectivity between the curves  $c^n$ , which possess a  $t_{2,2,2,2}$  and those quadruple tangents. The system  $[c^n]$  has as index  $(n-1)(n+4)(n-4)(n-5)(n-6)(n-7)$ <sup>3)</sup>, the tangents  $t_{2,2,2,2}$  form (§ 5) a system with index  $\frac{1}{3}n(n-4)(n-5)(n-6)(n-7)$ . The figure produced consists of twice the locus of the points of contact (§ 8) and the curve  $(S)$  of the intersections of the  $c^n$  with its quadruple tangents. For the order of  $(S)$  we now find  $\frac{1}{3}(n-4)(n-5)(n-6)(n-7)(7n^2+9n-12)-\frac{1}{3}(n-5)(n-6)(n-7)(30n^2+38n-192)$  or  $\frac{1}{3}(n-5)(n-6)(n-7)(n-8)(7n^2+7n-30)$ .

The correspondence  $(T_2, S)$  determines in the pencil of rays  $(M)$  a correspondence with characteristic numbers  $\frac{1}{3}(n-5)(n-6)(n-7)(n-8)(15n^2+19n-96)$  and  $\frac{1}{3}(n-5)(n-6)(n-7)(n-8)(7n^2+7n-30)$ . As the tangents  $t_{2,2,2,2}$  passing through  $M$  each represent  $4(n-8)$

<sup>1)</sup> N p. 941.

<sup>2)</sup> N p. 943.

<sup>3)</sup> N p. 941.

coincidences, we find that *the complex contains*  $(n-5)(n-6)(n-7)(n-8)(9n^2+37n-72)$  *curves with a tangent*  $t_{2,2,2,3}$ .

The correspondence  $(MS, MS')$  has as characteristic number  $\frac{1}{3}(n-5)(n-6)(n-7)(n-8)(n-9)(7n^2+7n-30)$ ; each tangent  $t_{2,2,2,2}$  passing through  $M$  represents  $(n-8)(n-9)$  coincidences. From  $\frac{2}{3}(n-5)(n-6)(n-7)(n-8)(n-9)[(7n^2+7n-30)-2n(n-4)]$  ensues that  $\frac{1}{3}(n-5)(n-6)(n-7)(n-8)(n-9)(n^2+3n-6)$  *curves of*  $\Gamma$  *possess a quintuple tangent*  $t_{2,2,2,2,2}$ .

**10.** The curves  $c^n$  with a twice osculating tangent  $t_{3,3}$  form a system with index  $\frac{3}{2}(n-4)(n-5)(n^2+7n-9)$ <sup>1)</sup>, their tangents  $t_{3,3}$  (§ 4) a system with index  $9n(n-4)(n-5)$ . The figure produced by these projective systems consists of three times the curve  $(R_3)_{3,3}$ , containing the points of contact (§ 6) and the locus of the points  $O$ , which each  $c^n$  has moreover in common with its  $t_{3,3}$ . For the order of  $(O)$  we find  $\frac{3}{2}(n-4)(n-5)(n^2+7n-9)+9n^2(n-4)(n-5)-3(n-5)(9n^2+39n+135) = \frac{3}{2}(n-5)(n-6)(3n^2+7n-21)$ .

The correspondence  $(MR_3, MO)$  has as characteristic numbers  $(n-5)(n-6)(9n^2+39n-135)$  and  $9(n-5)(n-6)(3n^2+7n-21)$ ; each  $t_{3,3}$  passing through  $M$  represents  $2(n-6)$  coincidences. From this we find, that *the complex contains*  $6(n-5)(n-6)(3n^2+29n-54)$  *curves with a tangent*  $t_{3,4}$ .

The correspondence  $(MO, MO')$  has as characteristic number  $\frac{3}{2}(n-5)(n-6)(n-7)(3n^2+7n-21)$  and possesses in each  $t_{3,3}$  passing through  $M$  an  $(n-6)(n-7)$ -fold coincidence. From this ensues that  $\Gamma$  possesses  $9(n-5)(n-6)(n-7)(2n^2+11n-21)$  *curves with a tangent*  $t_{3,3,2}$ .

**11.** The curves  $c^n$  with a tangent  $t_{4,2}$  form a system with index  $6(n-4)(n-5)(n^2+11n-14)$ <sup>2)</sup>, their tangents  $t_{4,2}$  (§ 1) a system with index  $16n(n-4)(n-5)$ . These projective systems produce a figure, composed of four times the curve  $(R_4)_{4,2}$ , see § 6, twice the curve  $(R_2)_{4,2}$ , see § 7, and the locus of the points  $S$ , which each  $c^n$  has moreover in common with its  $t_{4,2}$ .

For the order of  $(S)$  we find  $6(n-4)(n-5)(n^2+11n-14)+16n^2(n-4)(n-5)-4(n-5)(4n^2+46n-138)-2(n-5)(12n^2+40n-132) = (n-5)(n-6)(22n^2+70n-192)$ .

From  $(MR_4, MS)$  we find again the number of the  $t_{5,2}$  (§ 3), from  $(MR_2, MS)$  the number of the  $t_{3,4}$  (§ 10).

The symmetrical correspondence  $(MS, MS')$  produces *one* new characteristic number. Its characteristic number is apparently  $(n-5)(n-6)(n-7)(22n^2+70n-192)$ , while the  $16n(n-4)(n-5)$  lines  $t_{4,2}$

<sup>1)</sup> N p. 942.

<sup>2)</sup> N p. 938.

passing through  $M$  represent each  $(n-6)(n-7)$  coincidences. From the remaining ones we find, that  $\Gamma$  possesses  $(n-5)(n-6)(n-7)$   $(14n^2 + 102n - 192)$  curves with a tangent  $t_{4,2,2}$ .

**12.** Any point is, in general, node of one  $c^n$  belonging to  $\Gamma$ . We consider the system of the  $c^n$  having their node  $D$  on a straight line  $\alpha$ . The straight line connecting  $D$  with the arbitrary point  $P$ , intersects  $c^n$  moreover in  $(n-2)$  points  $E$ . The nodal curves of which a point  $E$  lies in  $P$  belong to the net with base-point  $P$ . Now the locus  $J$  of the nodes of the net (JACOBI'S curve) is a curve of order  $3(n-1)$ , with node in  $P$ . The locus  $(E)$  has therefore a  $3(n-1)$ -fold point in  $P$ ; so it is of order  $(4n-5)$ . In each intersection of  $(E)$  with  $\alpha$ , a  $c^n$  has a node  $D$ , of which one of the tangents  $d$  passes through  $P$ . Consequently the locus  $(D)_P$  of the nodes of which one of the tangents passes through  $P$  is a curve of order  $(4n-5)$  having a node in  $P$ . Hence a straight line passing through  $P$  contains moreover  $(4n-7)$  points  $D$ ; any straight line is therefore tangent in the node for  $(4n-7)$  nodal curves.

On a straight line  $l$  the tangents  $d$  of the nodal curves of which the node lies on  $\alpha$ , determine a symmetrical correspondence  $(L, L')$ ; its characteristic number is apparently  $(4n-5)$ . The intersection of  $\alpha$  and  $l$  represents two coincidences, for the  $c^n$ , which has a node there, determines two points  $L$  each coinciding with the corresponding point  $L'$ . The remaining coincidences are produced by coinciding tangents  $d, d'$ . So the locus  $(C)$  of the cusps (cusp-locus) of  $\Gamma$  is a curve of order  $4(2n-3)$ .

**13.** The curves  $(D)_P$  and  $(D)_Q$  see § 12, have the  $(4n-7)$  points  $D$  in common, for which  $PQ$  is one of the tangents. The remaining  $(4n-5)^2 - (4n-7) = 16n^2 - 44n + 32$  intersections are nodes of curves  $c^n$ , of which the lines  $d$  and  $d'$  pass through  $P$  and  $Q$ .

We now consider the system of the nodal  $c^n$ , of which a tangent  $d$  passes through  $P$ . The pairs of tangents  $d, d'$  determine on a straight line  $l$  a correspondence  $(L, L')$ . Any ray  $d$  is tangent for  $(4n-7)$  curves; to its intersection  $L$  correspond therefore  $(4n-7)$  points  $L'$ . Through  $L'$  pass  $(16n^2 - 44n + 32)$  tangents  $d'$ ; as many points  $L$  have been associated to  $L'$ . The coincidences of  $(L, L')$  form two groups; the first contains the  $(4n-5)$  points  $D$  situated on  $l$ , for which  $d$  passes through  $P$ . The remaining ones arise in consequence of  $d'$  coinciding with  $d$ ; the tangents in the cusps of the complex envelop therefore a curve of class  $(16n^2 - 44n + 30)$ .

14. To each nodal  $c^n$ , of which the node  $D$  lies on  $a$  we associate its tangents  $d, d'$ , and consider the figure produced by those projective systems. As the  $c^n$  passing through a point  $P$  form a net,  $3(n-1)$  nodal curves of the system in question pass through  $P$ . The index of the system  $[d, d']$  is, as appeared above,  $(4n-5)$ . To the produced figure the straight line  $a$  belongs six times. So the order of the locus of the points  $E$ , which  $c^n$  has moreover in common with  $d, d'$ , is a curve of order  $n(4n-5) + 6(n-1) - 6 = 4n^2 + n - 12$ .

For  $n=3$  we find 27; in this case  $(E)$  consists apparently of 27 straight lines. If  $T$  has six base-points, this result is confirmed as follows. Each  $c^n$  passing through 5 base-points intersects  $a$  in two points  $D$ ; the lines connecting these points with the 6<sup>th</sup> base-point form each with  $c^2$  a  $c^3$  of  $T$ , and belong to  $(E)$ ; in this way 12 straight lines are found. The connecting line  $b$  of two base-points cuts  $a$  in a point  $D$ , which determines with the remaining four base-points a  $c^2$ ; the 15 lines  $b$  belong apparently also to  $(E)$ .

The curve  $(E)$  cuts  $a$  in  $(4n-7)$  groups of  $(n-3)$  points  $E$  arising from the nodal curves which have  $a$  for tangent in their nodes. In each of the remaining intersections a nodal  $c^n$  has a three-point contact with one of its tangents  $d$ . From this ensues that *the locus  $(F)$  of the flecnodes is a curve of order  $(20n-33)$* .

In the above case  $n=3$  this figure consists of six conics and fifteen straight lines.

15. The tangents  $d, d'$  in the nodes of the nodal curves of a net envelop a curve of class  $3(n-1)(2n-3)^1$ . If the net has a base-point  $B$  there is a  $c^n$  having a node in  $B$ . Through  $B$  pass then  $3(n-1)(2n-3)-6$  tangents  $d$  of nodal curves of which the node does not lie in  $B$ . In order to understand this we consider a net of cubics with seven base-points. Through the base-point  $B$  pass no tangents of proper nodal curves. But the straight line connecting  $B$  with another base-point  $B'$ , forms with the  $c^2$  passing through the remaining base-points a binodal  $c^3$ ; the straight line  $BB'$  represents therefore two tangents  $d$ . For  $n=3$  we have  $3(n-1)(2n-3)=18$ ; as the 6 straight lines  $BB'$  represent 12 tangents  $d$ , the tangents  $d$  of the nodal  $c^3$  having its node in  $B$  are each to be counted thrice.

We now consider the system of the nodal curves  $c^n$ , which send one of their tangents  $d$  through  $P$ . Any ray passing through  $P$  is tangent  $d$  for  $(4n-7)$  curves (§ 12) and is moreover cut by those

<sup>1)</sup> Cf. for instance my paper "On nets of algebraic plane curves." (These Proceedings VII, 631-633).

curves in  $(4n-7)(n-3)$  points  $G$ . As base-point of a net belonging to  $\Gamma$   $P$  lies on  $(6n^2-15n+3)$  tangents  $d$  of nodal curves passing through  $P$ ; so the locus  $(G)$  has in  $P$  a  $(6n^2-15n+3)$ -fold point and is therefore of order  $(6n^2-15n+3) + (4n-7)(n-3) = 10n^2 - 34n + 24$ .

The correspondence  $(MD, MG)$  has as characteristic numbers  $(4n-5)(n-3)$  and  $(10n^2-34n+24)$ ; the ray  $MP$  represents  $(4n-7)(n-3)$  coincidences. As the remaining ones arise from coincidences  $D \equiv G$ , it ensues that *the inflectional tangents of the flecnodes envelop a curve of class  $(10n^2-32n+18)$* .

**16.** Let the complex be given by the equation

$$\alpha A + \beta B + \gamma C + \delta D = 0.$$

If the derivative of  $A$  with regard to  $x_k$  is indicated by  $A_k$  it ensues from the equations

$$\alpha A_k + \beta B_k + \gamma C_k + \delta D_k = 0 \quad (k = 1, 2, 3)$$

that an arbitrary point is node of *one*  $e^n$ , unless

$$\begin{vmatrix} A_1 & B_1 & C_1 & D_1 \\ A_2 & B_2 & C_2 & D_2 \\ A_3 & B_3 & C_3 & D_3 \end{vmatrix} = 0.$$

be satisfied.

The exceptional points in question  $K$  (*critical points*) are consequently common points of the four curves of JACOBI belonging to the nets  $\alpha = 0$ ,  $\beta = 0$ ,  $\gamma = 0$ ,  $\delta = 0$ .

To the intersections of  $|A_k B_k C_k| = 0$  with  $|B_k C_k D_k| = 0$  belong the points, for which we have

$$\begin{vmatrix} B_1 & B_2 & B_3 \\ C_1 & C_2 & C_3 \end{vmatrix} = 0$$

and they are not situated on the two other curves  $J$ . The last mentioned relation is apparently satisfied by  $2^2(n-1)^2 - (n-1)^2 = 3(n-1)^2$  points; consequently the number of *critical points* amounts to  $3^2(n-1)^2 - 3(n-1)^2$  or  $6(n-1)^2$ .

**17.** If  $\Gamma$  has a base-point  $B$  this is as base-point of any net of  $\Gamma$ , node of the curves  $J$ , consequently represents *four* points  $K$ . *The number of critical points of a complex with  $b$  base-points amounts therefore to  $6(n-1)^2 - 4b$ .*

Any point  $K$  is node of  $\infty^1$  curves forming a pencil, hence cusp of *two* curves; the cuspidal tangents are the double rays of the

involution formed by the pairs  $d, d'$ . So  $K$  is node of the locus  $(C)$  of the cusps.

All  $c^n$  passing through an arbitrary point  $P$  form a net,  $N$ . The curve  $J$  of  $N$  has a node in  $B$  and passes through all the points  $K$ ; for through  $B$  passes one  $c^n$  of the pencil of nodal curves determined by  $K$ . The curves  $(C)$  and  $J$  have two points in common in each point  $K$ ; they further intersect in the  $12(n-1)(n-2)$  cusps of  $N$ ; the remaining intersections are found in  $B$ . From  $4(2n-3)(3n-3) - 2[6(n-1)^2 - 4] - 12(n-1)(n-2) = 8$  it appears that the curve  $(C)$  has a quadruple point in  $B$ .

$B$  is node for all  $c^n$  of a pencil, consequently cusp of two  $c^n$ ; from this follows that each of the two cusptangents is touched by two branches of  $(C)$ .

Any point  $K$  is flecnode for five  $c^n$ . In order to understand this we consider the curve which arises if to each nodal  $c^n$  of the pencil  $(K)$  its tangents  $d, d'$  are associated. The  $c^{n+2}$  thus produced has with a line  $d$  only  $(n-3)$  points outside  $K$  in common.

The locus  $(F)$  of the flecnodes passes therefore five times through each of the critical points.

The locus  $J$  of the nodes in the net  $N$ , which is set apart from  $\Gamma$  by an arbitrary point  $P$ , has with  $(F)$  five intersections in each point  $K$ . They further have the  $3(n-1)(10n-23)$  flecnodes<sup>1)</sup> of  $N$  in common; the remaining intersections lie in the  $b$  base-points. From  $3(n-1)(20n-33) - 5[6(n-1)^2 - 4b] - 3(n-1)(10n-23) = 20b$  it appears that the curve  $F$  passes ten times through each of the base-points.

Each of the inflectional tangents  $f$  of the five  $c^n$ , having a flecnode in  $B$ , touches two of the branches.

**18.** The curves  $(C)$  and  $(F)$  have in the critical points  $K$  and the base-points  $B$  of  $\Gamma$   $10[6(n-1)^2 - 4b] + 40b$ , or  $60(n-1)^2$  points in common. Each of the remaining  $(20n-33)(8n-12) - 60(n-1)^2$  intersections is a cusp with a four-point tangent and at the same time to be counted twice as flecnode. In  $\Gamma$  occur therefore  $(50n^2 - 192n + 168)$  cusps with four-point tangent.

If we have  $n = 3$ ,  $b = 6$ , these particular curves are easy to determine. Any line  $BB'$  is tangent of two conics passing through the remaining four base-points; through each point  $B$  pass two tangents to the conic of the remaining five base-points. All in all

<sup>1)</sup> N p. 944.

we find therefore  $15 \times 2 + 6 \times 2 = 42$  figures  $(c^2, c^1)$ , satisfying the condition.

The tangents in a flecnode we shall indicate by  $f$  and  $d$ ;  $f$  indicates the inflectional tangent. We shall determine the index of the system  $[d]$ .

The curve  $(D)_P$ , containing the nodes which send one of their tangents through  $P$  (§ 12), passes through the points  $K$  and twice through the points  $B$ . With  $(F)$  it has, apart from those points,  $(4n-5)(20n-33)-30(n-1)^2$  or  $50n^2-172n+135$  intersections. As many tangents  $f$  and  $d$  pass through  $P$ . The number of lines  $f$  amounts according to § 15 to  $(10n^2-32n+18)$ , hence  $[d]$  has as index  $(40n^2-140n+117)$ .

In order to find the locus of the points  $G$ , which any flecnodal  $c^n$  has in common with its tangent  $d$  we consider the product of the projective systems  $[c^n]$  and  $[d]$ . Their indices are  $3(n-1)(10n-23)$ , i.e. the number of flecnodal  $c^n$  in a net, and  $(40n^2-140n+117)$ . Since the curve  $(F)$  belongs three times to the figure produced, we find for the order of  $(G)$   $3(n-1)(10n-23) + n(40n^2-140n+117) - 3(20n-33)$  or  $(40n^3-110n^2-42n+168)$ .

Let us now consider the correspondence  $(MF, MG)$ . The straight lines  $d$  passing through  $M$  produce each  $(n-3)$  coincidences; the number of the remaining ones amounts to  $(20n-33)(n-3) + (40n^3-110n^2-42n+168) - (40n^2-140n+117)(n-3) = 170n^2-672n+618$ .

To the coincidences  $F \equiv G$  determined by this belong in the first place the cusps with tangent  $t_4$ ; the remaining ones arise in pairs from nodal curves with two inflectional tangents  $f$ . Their number amounts therefore to  $\frac{1}{2} [(170n^2-672n+618) - (50n^2-192n+168)]$ ; *the complex contains  $(60n^2-240n+225)$  curves with a fleflecnode.*

In the case  $n=3$ ,  $b=6$  we find 45 for it. Each of the trilaterals belonging to  $F$  is apparently to be considered as a figure with three fleflecnodes.

**19.** In a similar way as in N § 5, 13, 14 it may be determined how many times a base-point  $B$  of the complex is point of contact of a particular tangent. We find then in the first place that  $B$  is point of contact  $R_5$  of ten tangents  $t_5$ . It is further consecutively found that  $B$  is point of contact  $R_4$  of  $(n-5)(n+16)$  tangents  $t_{4,2}$ , point of contact  $R_3$  of  $3(n-5)(n+6)$  tangents  $t_{3,3}$  and of  $2(n-5)(n-6)(n+6)$  tangents  $t_{3,2,2}$ , point of contact  $R_2$  of  $2(n-5)(3n+8)$  tangents  $t_{2,4}$ , of  $3(n-5)(n-6)(3n+8)$  tangents  $t_{2,3,2}$ , and  $\frac{2}{3}(n-5)(n-6)(n-7)(3n+8)$  tangents  $t_{2,2,2,2}$ .

**Physics.** -- "*The diffusion-coefficient of gases and the viscosity of gas-mixtures.*" By Prof. J. P. KUENEN. (Communications from the Physical Laboratory at Leiden. Suppl. 38).

In two previous communications<sup>1)</sup> on the same subject it was shown to what cause the difference between the results of the two current theories of gas-diffusion is to be ascribed. Whereas MAXWELL'S theory (STEFAN, LANGEVIN, CHAPMAN<sup>2)</sup>) leads to the result, that the coefficient of diffusion is independent of the proportion in which two gases are mixed, O. E. MEYER'S theory which uses the method of the molecular free path gives a coefficient which changes with the composition of the mixture. For two gases whose molecules have masses  $m_1$  and  $m_2$  the coefficient of diffusion lies between two limiting values which are to each other in the proportion  $m_1 : m_2$ . The coefficient of diffusion for carbon-dioxide ( $M_1 = 44$ ) with a trace of hydrogen ( $M_2 = 2$ ) would be 22 times larger than that of hydrogen with a trace of carbon-dioxide; between those limiting values  $D$  would diminish regularly with the composition.

The cause of this difference between the two results is due to the circumstance, that in O. E. MEYER'S theory no account is taken of the "persistence" of molecular motion which was introduced into the kinetic theory by JEANS<sup>3)</sup>. The persistence consists in that a molecule, when colliding with another, retains on the average a component of velocity in the direction of its motion before the collision, so that after a collision all directions are not, as used to be generally assumed, equally probable. The manner in which JEANS corrects O. E. MEYER'S formula for the persistence is incorrect, however, and does not lead to a better result, because he takes for the persistence the value derived by him for a single gas, whereas the persistence in a mixture should have been introduced. In the previous papers cited above it was shown, that by doing the latter, the formula is modified in such a way, that the strong contradiction with the result of the other theory disappears.

Qualitatively the matter may be put as follows. Let us first consider carbon-dioxide with a trace of hydrogen; the theory shows that in this mixture  $D$  is determined by the mobility and by the free path of the hydrogen-molecules which are both relatively large,

<sup>1)</sup> J. P. KUENEN. These Proc. 15. p. 1152. 1913. 16. p. 1162. 1914. Comm. Leiden, Suppl. 28, 36.

<sup>2)</sup> S. CHAPMAN, Phil. Trans. 211 A p. 433. 1912; this article which was not mentioned in the previous papers may be specially referred to on this occasion.

<sup>3)</sup> J. H. JEANS Dyn. Theory of gases. 1904. p. 236. seq.

viz. the former inversely proportional to  $\sqrt{m_2}$  and the latter proportional to  $\sqrt{m_1}$ , so that  $D$  is proportional to  $\sqrt{\frac{m_1}{m_2}}$ . Similarly for a trace of carbon-dioxide in hydrogen  $D$  is proportional to  $\sqrt{\frac{m_2}{m_1}}$ , so that the ratio of the two coefficients is as  $m_1 : m_2 = 44 : 2$ . When the persistence is taken into account the ratio becomes quite different: the persistence is much smaller for the light hydrogen-molecules than for the heavy carbon-dioxide molecules, the consequence being, that the diffusion-coefficient is much less increased by the correction in the former than in the latter case. With the value given for the persistence in the papers mentioned the compensation was even complete, so that  $D$  for  $n_1 = 0$  became equal to  $D$  for  $n_2 = 0$ , whereas for intermediate mixtures  $D$  obtained other values.

Quite recently Miss A. SNETHLAGE, student of physics at Amsterdam, who is engaged on an investigation of various applications of the persistence-theory, has drawn my attention to the fact, that the expression given by me for the persistence cannot be correct. For, whereas for the case, that the masses  $m_1$  and  $m_2$  of the molecules are equal, it gives correctly the expression found by JEANS, on the other hand for  $m_2$  infinite it gives a negative value, although a simple calculation shows that its value must be nought in this case.

In repeating the calculation it was found that on the former occasion an error had crept in which would have been noticed before, if the agreement with JEANS's value for  $m_1 = m_2$  had not erroneously been taken as a proof of its being correct. The present calculation yielded the following expression for the mean persistence of a molecule  $m_1$  colliding with a molecule  $m_2$ :

$$\mathfrak{D}_1 = \frac{m_1}{2(m_1 + m_2)} + \frac{1}{4} \frac{m_1^2}{m_2^{1/2}(m_1 + m_2)^{3/2}} \log \frac{\sqrt{(m_1 + m_2)} + \sqrt{m_2}}{\sqrt{(m_1 + m_2)} - \sqrt{m_2}},$$

which is identical with that found by miss SNETHLAGE. The calculation may be shortly reproduced; with a view to an easy comparison with JEANS his notation and also, as far as possible, his method of calculation will be used.

We take two molecules with definite velocities  $a$  and  $b$ , which collide in all possible ways, and calculate for molecule  $a$  the mean velocity after the collision taken in the original direction of its motion. MAXWELL has proved, that this velocity is equal to that of the centre of mass projected on the same direction. Calling the angle between  $a$  and  $b$   $\mathfrak{D}$ , this projection  $p$  is given by

$$p = \frac{am_1 + bm_2 \cos \mathfrak{D}}{m_1 + m_2}.$$

This projection has now to be averaged for all angles  $\vartheta$ , taking into account, that the chance of a collision for each direction is proportional to the relative velocity  $r$  and to  $\frac{1}{2} \sin \vartheta d\vartheta$ . The mean is therefore given by

$$\frac{\int_0^{\pi} p r \sin \vartheta d\vartheta}{\int_0^{\pi} r \sin \vartheta d\vartheta}$$

As  $r^2 = a^2 + b^2 - 2ab \cos \vartheta$ , it follows, that  $r dr = ab \sin \vartheta d\vartheta$ . After substitution of  $\sin \vartheta d\vartheta$  and of  $p$  and integration we obtain

$$\frac{(2m_1 + m_2) a^2 + m_2 b^2}{2(m_1 + m_2) a} \frac{m_2}{m_1 + m_2} \frac{3}{10 a} \frac{5 a^4 + 10 a^2 b^2 + b^4}{3 a^2 + b^2} \text{ for } a > b$$

and

$$\frac{(2m_1 + m_2) a^2 + m_2 b^2}{2(m_1 + m_2) a} \frac{m_2}{m_1 + m_2} \frac{3}{10 a} \frac{a^4 + 10 a^2 b^2 + 5 b^4}{a^2 + 3b^2} \text{ for } a < b;$$

these expressions have to replace those given by JEANS (i.e. p. 239). With JEANS we may put  $a = \kappa b$ .

The chance per second, that a molecule with velocity  $a$  collides with a molecule with velocity  $b$ , the relative velocity being  $r$ , is

$$2 n_2 \sigma \sqrt{\pi h^3 m_2^3} e^{-hm_2 b^2} \frac{b}{a} db r^2 dr,$$

where  $n_2$  is the number of molecules  $m_2$  per unit volume, and as the number of molecules per unit volume with velocity  $a$  is equal to

$$4 n_1 \sqrt{\frac{h^3 m_1^3}{\pi}} e^{-hm_1 a^2} a^2 da$$

( $n_1 =$  total number of molecules  $m_1$  per unit volume), the total number of collisions of the kind considered will be

$$8 n_1 n_2 \sigma^2 h^3 \sqrt{m_1^3 m_2^3} e^{-h(m_1 a^2 + m_2 b^2)} ab da db r^2 dr.$$

Integrated with respect to  $r$  for  $a > b$ , when the limits of  $r$  are  $a + b$  and  $a - b$ , this becomes

$$\frac{16}{3} n_1 n_2 \sigma^2 h^3 \sqrt{m_1^3 m_2^3} e^{-h(m_1 a^2 + m_2 b^2)} ab^2 (a^2 + b^2) da db$$

and similarly for  $a < b$

$$\frac{16}{3} n_1 n_2 \sigma^2 h^3 \sqrt{m_1^3 m_2^3} e^{-h(m_1 a^2 + m_2 b^2)} a^2 b (a^2 + 3b^2) da db.$$

In both expressions we may again put  $a = \kappa b$ .

To find the mean persistence the above expressions for the number of collisions have to be multiplied each by the corresponding mean persistence, separately for  $a > b$  and  $a < b$ , then to be integrated with respect to  $b$  between 0 and  $\infty$ , further with respect to  $z$ , in the former case between 1 and  $\infty$  and in the latter between 0 and 1, and finally to be divided by the total number of collisions:

$$2 n_1 n_2 \sigma^2 \sqrt{\frac{\pi (m_1 + m_2)}{h m_1 m_2}}.$$

The result of this somewhat lengthy calculation which need not be detailed any further was given above. A corresponding expression is found for the  $m_2$ -molecules viz.

$$\vartheta_2 = \frac{m_2}{2(m_1 + m_2)} + \frac{1}{4} \frac{m_2^2}{m_1^{1/2} (m_1 + m_2)^{3/2}} \log \frac{\sqrt{(m_1 + m_2)} + \sqrt{m_1}}{\sqrt{(m_1 + m_2)} - \sqrt{m_1}}.$$

The formulae given before for the *coefficient of diffusion* are now somewhat modified. Qualitatively there is no change, but the compensation at the limits referred to above is not so complete as before.

For  $D$  the same expression holds as before viz.:

$$D = \frac{1}{3n} (n_2 u_1 l_1 f_1 + n_1 u_2 l_2 f_2),$$

where  $l_1$  and  $l_2$  keep their meaning, viz.:

$$l_1 = 1 : \left\{ \sqrt{2} n_1 \pi s_1^2 \left( 1 + \frac{C_1}{273} \right) + n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \left( 1 + \frac{C_{12}}{273} \right) \right\}$$

and

$$l_2 = 1 : \left\{ \sqrt{2} n_2 \pi s_2^2 \left( 1 + \frac{C_2}{273} \right) + n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \left( 1 + \frac{C_{12}}{273} \right) \right\},$$

but

$$f_1 = 1 : \left\{ 1 - \sqrt{2} n_1 \pi s_1^2 \left( 1 + \frac{C_1}{273} \right) l_1 \times 0.406 - n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \left( 1 + \frac{C_{12}}{273} \right) l_1 \vartheta_1 \right\}$$

and

$$f_2 = 1 : \left\{ 1 - \sqrt{2} n_2 \pi s_2^2 \left( 1 + \frac{C_2}{273} \right) l_2 \times 0.406 - n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \left( 1 + \frac{C_{12}}{273} \right) l_2 \vartheta_2 \right\},$$

For  $n_1 = 0$  and  $n_2 = 0$  we now obtain:

$$D(n_1 = 0) = \frac{2}{3n \pi \sigma^2} \sqrt{\frac{m_2}{\pi h m_1 (m_1 + m_2)}} \left( 1 + \frac{C_{12}}{273} \right) \frac{1}{1 - \vartheta_1}$$

and

$$D(n_2=0) = \frac{2}{3n\pi\sigma^2} \sqrt{\frac{m_1}{\pi h m_2(m_1+m_2)}} \left(1 + \frac{C_{12}}{273}\right) \frac{1}{1-\vartheta_2},$$

the ratio of which is:

$$\frac{D(n_1=0)}{D(n_2=0)} = \frac{m_2}{m_1} \frac{1-\vartheta_2}{1-\vartheta_1}.$$

Calculation gives for the persistence of carbon-dioxide in relation to hydrogen 0.942, for that of hydrogen in carbon-dioxide 0.239, so that for these two gases the above ratio becomes 0.77. According to the theory as corrected the ratio is therefore still much nearer unity than according to the uncorrected theory of O. E. MEYER which gives  $\frac{2}{34} = 0.045$  in this case. As a complete agreement with MAXWELL'S theory is in any case lacking, the remaining difference between the two limiting values is not of any special consequence and no useful purpose would be served by communicating further numerical results. With combinations of gases which differ less in molecular weight the difference between the limiting values is smaller.

The formula for the *viscosity of a gas-mixture* undergoes a corresponding modification. As before the relation holds:

$$\eta = 0.35 \frac{n_1}{n} d_1 u_1 l_1 f_1' + 0.35 \frac{n_2}{n} d_2 u_2 l_2 f_2',$$

where  $f_1'$  and  $f_2'$  now have the values:

$$\begin{aligned} f_1' = 1 : & \left\{ 1 - \frac{1}{2} \sqrt{2} n_1 \pi s_1^2 \left(1 + \frac{C_1}{273}\right) l_1 \times 0.406 - \right. \\ & \left. - \frac{m_1}{m_1 + m_2} \times n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \left(1 + \frac{C_{12}}{273}\right) l_1 \vartheta_1 \right\} \\ f_2' = 1 : & \left\{ 1 - \frac{1}{2} \sqrt{2} n_2 \pi s_2^2 \left(1 + \frac{C_2}{273}\right) l_2 \times 0.406 - \right. \\ & \left. - \frac{m_2}{m_1 + m_2} \times n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \left(1 + \frac{C_{12}}{273}\right) l_2 \vartheta_2 \right\}. \end{aligned}$$

The numerical values which are now found for mixtures of carbon-dioxide and hydrogen, and of argon and helium respectively are somewhat lower than before, but the maxima which had to be explained by the theory remain. For the former pair of gases calculation for  $n_1 = n_2 = \frac{1}{2} n$  gives  $\eta = 0.0001470$  (observed 144), for the latter pair  $\eta = 0.0002306$  for  $n_1 = n_2 = \frac{1}{2} n$  and  $\eta = 0.0002281$  for  $n_1 = \frac{3}{5} n$ ,  $n_2 = \frac{2}{5} n$ , which results differ even a little less from the observed maximum 0.0002207 than according to the former calculation.

## ERRATA.

In the Proceedings of the Meeting of September 26, 1914:

p. 528 line 9 and 10 from the top: For: "On plate IA of Comm. N<sup>o</sup>. 107 $\alpha$  may be seen that part of the apparatus" read: "Part of the apparatus of Plate I A of Comm. N<sup>o</sup>. 107 $\alpha$  is similar to that of our apparatus";

p. 532 line 6 from the bottom: for "the radius of molecular action is larger" read: "the sphere of molecular action reaches in the liquid to further layers of surrounding molecules".

In the Proceedings of the Meeting of December 30, 1914: p. 905 line 6 from the top: for 90 $\pm$  read 900.

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February 27, 1915.



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C O N T E N T S.

- S. DE BOER: "On the heart-rhythm". (Communicated by Prof. J. K. A. WERTHEIM SALOMONSON), p. 1075.  
K. KUIPER JR.: "The physiology of the air-bladder of fishes". (Communicated by Prof. MAX WEBER), p. 1088.  
Miss ADA PRINS: "On critical end-points and the system ethane-naphtalene". (Communicated by Prof. A. F. HOLLEMAN), p. 1095.  
JAN DE VRIES: "Systems of circles determined by a pencil of conics", p. 1107.  
F. A. H. SCHREINEMAKERS and Miss W. C. DE BAAT: "Compounds of the arsenious oxide" I, p. 1111.  
ERNST COHEN and S. WOLFF: "The allotropy of potassium" I, p. 1115.  
H. A. VERMEULEN: "The vagus area in camelidae". (Communicated by Prof. L. BOLK), p. 1119.

**Physiology.** — "*On the heart-rhythm*". By Dr. S. DE BOER. (Communicated by Prof. Dr. WERTHEIM SALOMONSON).

(Communicated in the meeting of Jan. 30, 1915).

1. *The a-v-interval and the refractory period.*<sup>1)</sup>

The normal heart-rhythm is caused by a system of different factors, among which the irritability and the transmission of stimulation of the different parts of the heart are of great significance. I have now made a series of experiments on frogs, in which I have modified these two principal properties of the heart by means of veratrine. I followed in my experiments this method: the heart was suspended on the point, after I had removed the sternum, cut open the pericardium and cut the frenulum in two. The single suspension was used, because I intended to note down, after the poisoning, during

<sup>1)</sup> The experiments mentioned here were communicated by me in a lecture, held in the meeting of the biological section of the Genootschap ter bevordering der Natuur-, Genees- en Heelkunde at Amsterdam of November 19<sup>th</sup> 1914.

a couple of hours and longer, all systoles; this aim can be better reached with one lever than with two. By doing so I had to watch only one friction on the smoked paper, when noting down the systoles of the auricles and ventricles, so that their succession, with regard to time, can be better estimated and we obtain a better survey of the whole reproduction. The curves were noted down by the lever on an endless smoked paper which was wound round three kymographia; the motion was obtained in the usual way by making one of these apparatuses turn, whilst the two others with unscrewed axes followed the revolution. In this way I could note down during two hours and a half after the poisoning all the curves and obtained the entire reproduction of the poisoning; in order to make a comparison first about one hundred systoles of the unpoisoned heart were reproduced. To a maximum of ten drops of 1% acetas veratrini were then injected into the abdominal cavity. About 10 minutes after the injection the systoles became larger and wider, the a-v-interval increased, the electric irritability of the ventricle diminished. When I fixed before the poisoning the weakest stimulation with which I could obtain an extra-systole after the beginning of the diastole, I had, after the poisoning, either to strengthen it or to apply it later, in order to obtain the same effect. This continued till in the end, during the whole diastole, I did not obtain any effect on the ventricle not even with the strongest stimulation.

In this stage of the poisoning I observed quite a new phenomenon: at the end of the diastole no extrasystole was obtained after irritation, but a pause of the ventricle. The duration of this pause was always of such a nature that, added to the duration of the preceding heartperiod, they amounted together to two heart-periods. The pause began with an extrasystole of the auricle. The auricle was now irritable indeed, which was promoted by lengthening the a-v-interval. This extrasystole of the auricle was caused by retrogressive transmission of stimulation or with strong stimulation by current-loops.

The next-following irritation coming from the sinus venosus finds then the auricle refractory. The result is that one auricle- but likewise one ventricle-systole falls out of the normal rhythm, and so an extra pause takes place. Now it is remarkable to see, how strongly widened the postcompensatory systoles are after these extra-pauses without extra-systoles. This fact is indeed entirely in accordance with the law on the conservation of the energy of the heart (LANGENDORFF). In my case indeed pause of the ventricle i. e. rest of the ventricle appears without preceding extra-systole. The condi-

tions for the formation of a postcompensatory systole as wide as possible (according to LANGENDORFF) are then most favourable.

The irritability of the heart-muscle during the diastole has much improved again during the pause. This appears from the fact, that the next-following systole, after the postcompensatory one, occurs in the diastole of this postcompensatory systole. The ventricle consequently is now susceptible of the weak physiological irritation coming from the auricle, whilst, two heart-periods before during the diastole, it was still insusceptible of a much stronger, artificial stimulation. By artificial irritation in the diastole of the post-compensatory curve I could again bring about extra-systoles, which did not occur when, with the same strength of stimulation, I irritated at the same moment of the diastole in the normal rhythm. The refractory period however can be enlarged during this great systole without extending to the diastole. Experiments, in which I noted likewise the action-currents, taught me, that during the extra-pause the ventricle neither produced action-current.

I repeated this experiment more than a hundred times. An extra-stimulation occurring somewhat later caused again an extra-systole (vide Fig. 1 the 7<sup>th</sup> systole of the second curveseries).

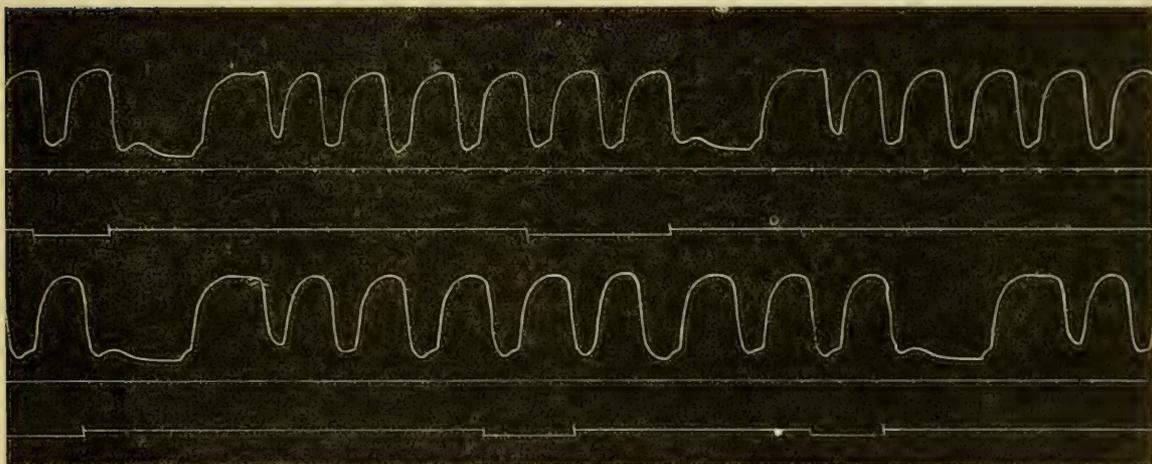


Fig. 1.

In a later period of the poisoning the rhythm of the ventricle is halved, after the extent of the systoles has first diminished. The cause of this phenomenon lies in the prolongation of the refractory period and of the a—v-interval. An auricle systole falls consequently at last in the refractory period of the preceding ventricle-systole, so that then every 2<sup>nd</sup> auricle-systole remains unanswered by the ventricle.

Both of auricle and ventricle the halving of the rhythm can also suddenly occur (i. e. with regard to the sinus-contractions).

After this rhythm-halving the a-v-interval is shortened again, the irritability of the ventricle has improved: an extra-stimulation during the diastole causes again an extra-systole, but now without compensatory pause; the row of the ventricle-curves has only been removed by one auricle-systole. The duration of this extra-period + the duration of the preceding period is now equal to the duration of  $1\frac{1}{2}$  heart-periods.

When now this halved rhythm of the ventricle has existed for a short time, I can, with one induction-stroke during the diastole, reduce this rhythm to the original one, which can continue again for some time: consequently an artificial return to the original rhythm. This experiment can be explained as follows: In the first place it is irrefutable, that the metabolic condition of the heartmuscle was such as to allow the heart to pulsate in the normal rhythm; nor were the physiological irritations proceeding from the auricle wanting, for only the ventricle pulsated in the halved rhythm; and yet this halved rhythm would have continued, if I had not intervened by an extra-stimulation. The cause of this phenomenon is, that the systoles of the halved type are much larger and wider than those of the not halved one. Each systole in itself of the halved type has consequently a larger refractory period, so that each second auricle-systole cannot be answered by the ventricle. The ventricle is consequently, as it were imprisoned in its own rhythm; if there were only one narrower systole with a smaller refractory period between, then the normal rhythm would have been restored with the smaller systoles. Now I obtain this little systole as an answer to the extra-stimulation, and because the latter took place directly after an auricle-systole, the extra-systole is not followed by a compensatory pause, but after the extra-stimulation I detect a continual recovery of the original rhythm. If the extra-systole was followed by a compensatory pause, this recovery of the rhythm could not take place, for the postcompensatory systole would have been enlarged (= widened) again, and would thus restore again the halved rhythm. At the same time we have here consequently before us an example of an extra-systole without a compensatory pause. The ventricle can thus again pulsate e. g. about 5 minutes in the original rhythm and then pass again in the ordinary way into the halved rhythm. During the first time of halving the metabolic condition of the heartmuscle had certainly much improved, but every large systole of this type has in itself a larger refractory period than every little systole of the

normal rhythm. The pauses in the latter rhythm, however, are much shorter, so that after some time the refractory period, at a given moment, after a systole of the ventricle, no longer depends only upon the preceding systole; for on account of the insufficient restoration between the quick heart-periods the preceding systoles have also had influence upon it; the refractory period increases again in such a way, that once more a halving of the ventricle-rhythm takes place. I could also bring about this change artificially, by intervening exactly in the same manner, by which I could alter the halved rhythm. By an extra-stimulation during or a short time after the diastole I made an extra-systole; this was followed by a compensatory pause, after which the post-compensatory systole, as always, is enlarged and widened. The enlarged refractory period is the cause that the halved rhythm returns again, because the first-following auricle-systole takes now again place in this refractory period. I could consequently these variations of rhythm bring about discretionally when the ventricle-rhythm had been halved for some time.

I practised a second method of variation of rhythm according to a quite different principle and with as certain a result. When the ventricle pulsated after the veratrine-poisoning in the halved rhythm, I could by refrigeration of the sinus venosus make the impulses, originating in the latter, reach the ventricle in a slower tempo. Thus every second auricle-systole moved over the refractory period of the preceding ventricle systole, and restoration of the original ventricle-rhythm was the result. As a transition I obtained then heart-bigeminy and trigeminy. Consequently we obtained here by refrigeration of the sinus venosus an increase of the frequency of the ventricle, this is an exception to GASKELL's experiment which teaches us, that refrigeration causes a decrease of the rhythm. Calefaction of the sinus venosus causes, after the preceding experiment, a return of the rhythm to the halved one.

Another method of bringing about variations of rhythm is calefaction and refrigeration of the ventricle. Calefaction of the ventricle shortens the refractory period, and changes consequently the halved rhythm into the normal one; refrigeration of the ventricle causes then again a restoration of the halved rhythm. I could most quickly change the halved rhythm of the ventricle into the normal one by refrigerating the sinus venosus, and at the same time calefying the ventricle. Especially by this latter method the variation of the rhythm succeeds always. The variation by an induction-stroke succeeds only, when the halved rhythm has not yet existed a long time, or when at the reaction of the poisoning, the halved rhythm was to change

again after the lapse of not too long a time into the not halved one.

I saw also repeatedly variations of rhythm occur spontaneously. When the poisoning-process increased these variations of rhythm resulted in the halved rhythm, which by further halvings applied to 1 ventricle-systole caused 4, 8 or sometimes 5, 6, or 7 auricle-systoles. At the reaction of the poisoning during the halving period these variations of rhythm are accompanied with varying lengthening and shortening of the a-v-interval. The lengthening occurs during the quick rhythm, the shortening by restoration during the slowly halved rhythm.

When the poisoning continues, no restoration takes place, but through lengthening of the a-v-interval and the refractory period further halving is the necessary result.

## 2. *The transmission of stimulation in the ventricle.*

We have seen that by poisoning with veratrine the transmission of stimulation between auricle and ventricle slackens. The mechanograms do not tell us anything about the transmission of the stimulation in the ventricle-muscle itself. In order to obtain more information about this subject I reproduced the action-currents before and at fixed times after the poisoning.

In Fig. 2 we have the suspension-curve and the electrogram of a not poisoned frog's heart. Time in  $\frac{1}{4}$  sec. Electrodes auricle-ventricular.

Whilst leaving for the rest all the circumstances the same, I make 12 minutes after the injection of 5 drops 1% acet. veratrine (vide Fig. 3) another reproduction.

The R-top is raised and widened, it is somewhat split.

The T-top has become positive, the line of connection between R and the T is lowered. The heartrhythm has slackened. The pauses between the mechanograms have lengthened, but those between the electrograms have shortened. The electrograms before the poisoning lasted till the beginning, after the poisoning till the end of the diastole; the duration of the electrograms runs parallel with the duration of the refractory period.

Both are indications of the metabolic processes of the heart-muscle. After the poisoning the beginning of the R-oscillation goes much more in advance of the suspension-curve than before the poisoning. The period of the latent irritation has consequently considerably lengthened after the poisoning.

Directly after the halving of the ventricle-rhythm, 1 hour 20 min. after the injection I obtain the representation of Fig. 4.

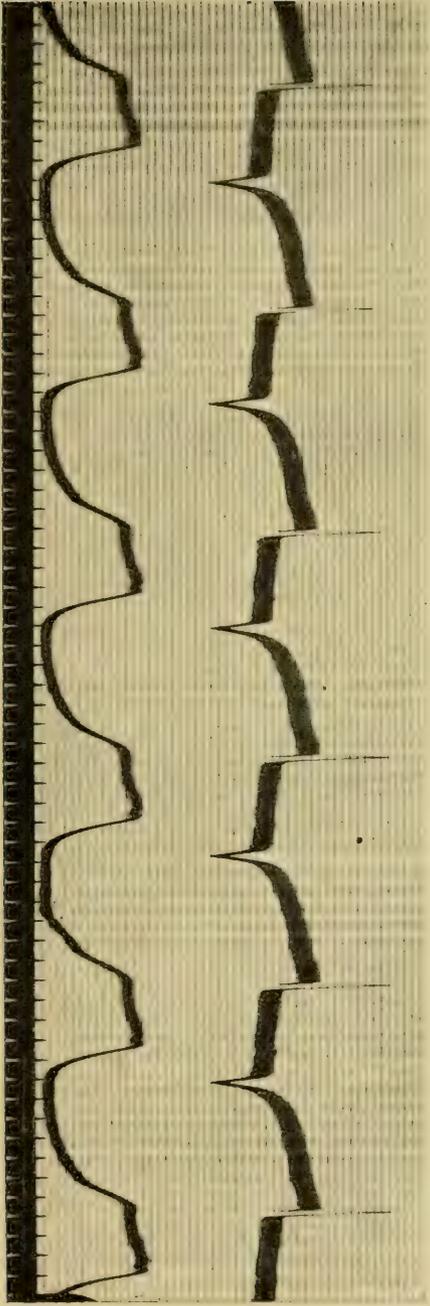


Fig. 2.

In Fig. 2, 3, 4, 5, 6, 7, 9, and 10 the time is at the top in  $\frac{1}{5}$  sec.; then follows the suspension curve with the top directed towards the time; at the bottom the oscillations of the string (the negativity of the basis shows in all the curves an oscillation of the time, consequently downward).

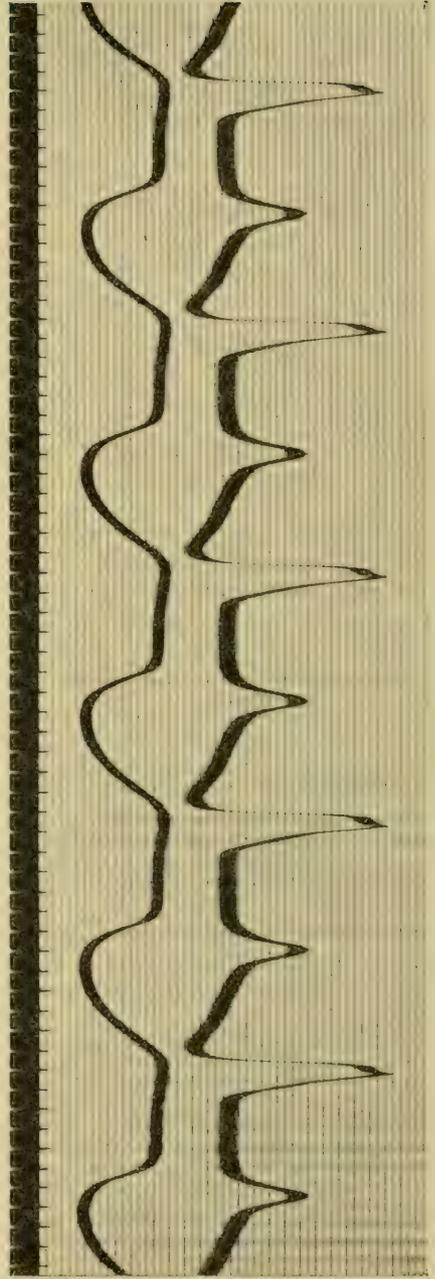


Fig. 3.

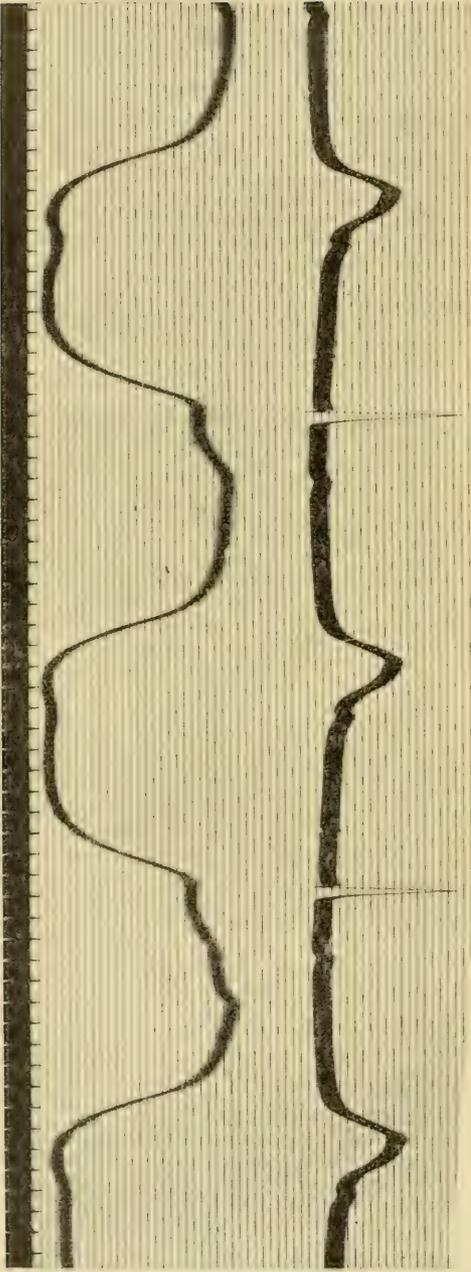


Fig. 4.

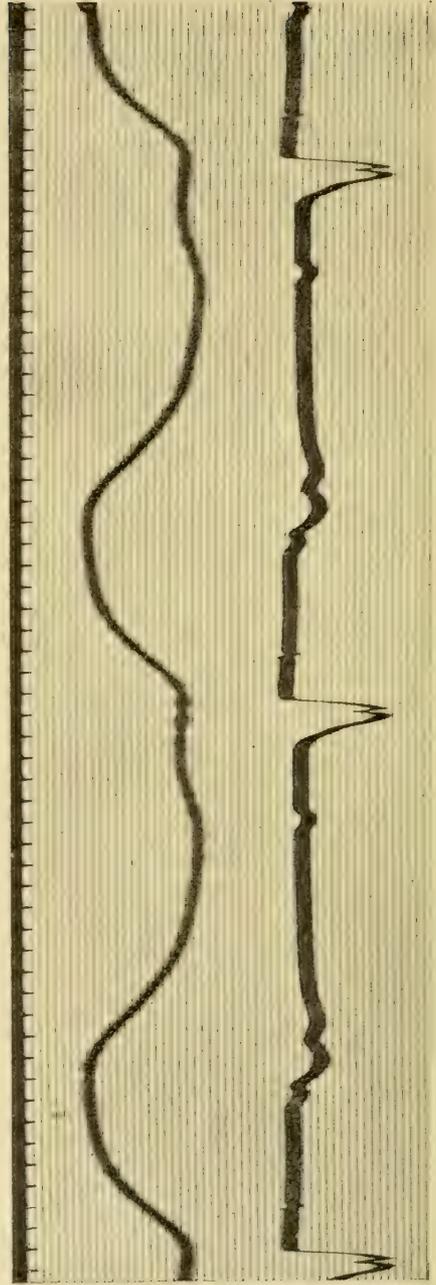


Fig. 5.

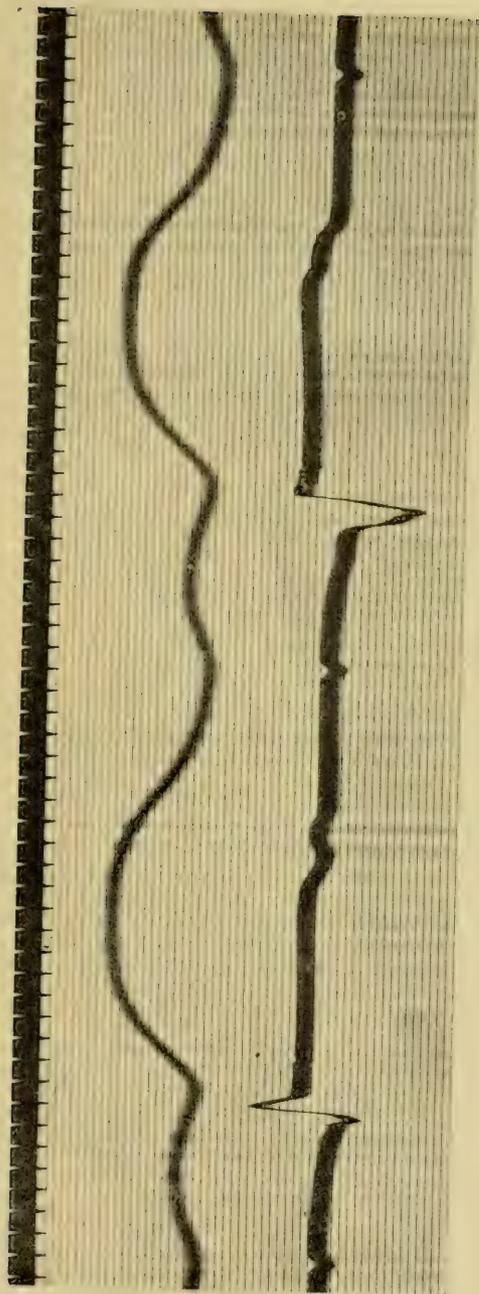


Fig. 6.

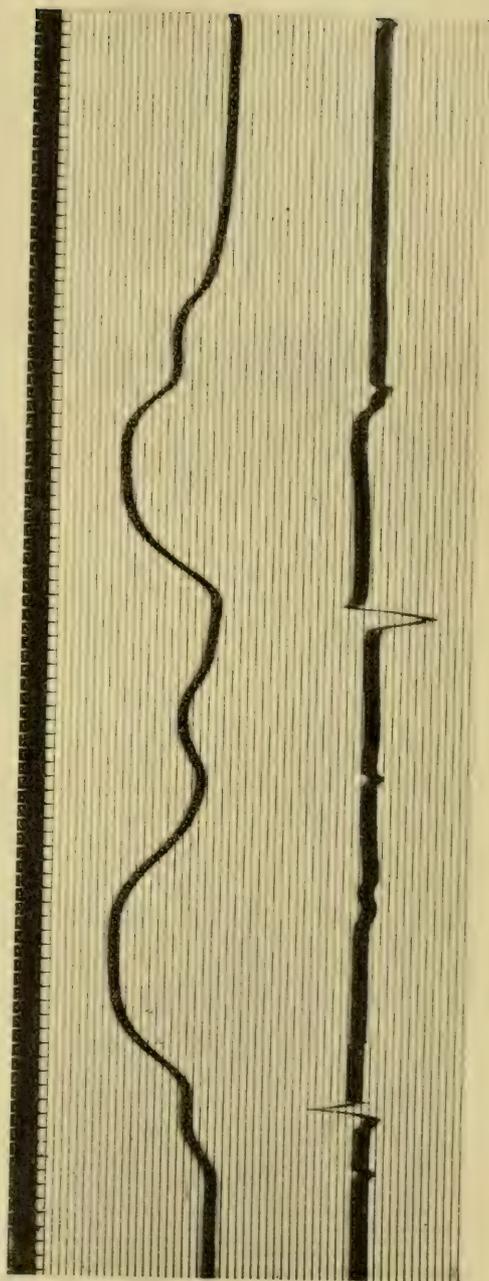


Fig. 7.

We see that with the restoration of the metabolic condition of the heart-muscle the variations indicated above have for the greater part regressed again. I call only the attention to the shorter duration of the R-oscillation. The a-v-interval is even again shorter than before the poisoning. Slackening of rhythm promotes shortening, poisoning lengthening of this interval.

Directly after the halving shortening prevails.

35 minutes after the reproduction of Fig. 4 I obtain representation Fig. 5. The R-branch has widened and split again, the a-v-interval has increased, and likewise the period of the latent irritation.

If now, in analogy with the duration of the action-currents for the striped muscles, we see in the duration of the R-oscillation a measure for the speed of the transmission of stimulation in the heart-muscle, then the variation of the duration of the R-oscillation becomes immediately intelligible. Through the poisoning the speed of the transmission of stimulation decreases, after the halving it improves again in the beginning, when the poisoning continues, the transmission falls afterwards off again into this halved rhythm.

We saw before, that the irritability of the heart muscle sustains the same oscillations during the poisoning and the halving-process. This cannot be otherwise, for transmission of stimulation means, that a level that is in irritation influences an adjacent level. The speed with which this influence can take place depends upon the irritability.

In a following period of the poisoning the basis and the point of the ventricle palpitate alternatively stronger (Vide Fig. 6). The a-v-time has increased again.

If now 25 minutes later I make another reproduction (vide Fig. 7) every 3<sup>rd</sup> systole has fallen out. In Fig. 7 we see consequently a bigeminusgroup, the point and the basis of which pulsate alternatively. With the naked eye this could be distinctly observed. We see after the long pause a short a-v-interval, after a short pause a long a-v-interval. On my suspension-curves of heart-bigeminy and -trigeminy, after veratrine-poisoning, of which I possess a great number, the increase of the a-v-interval in the bi- and trigeminus- groups can be observed. As an example I give Fig. 8.

I have asked myself if we have here a strict, legal proportion. Is the transmission of stimulation after a long pause always better than after a short one?

With a quite different intention I have now made an extensive investigation concerning the potential differences occurring in the heart at extra-systoles. In a series of experiments I irritated the

auricle for this purpose. I could consequently make use of these curves for the measurements, and now I find the a-v-interval

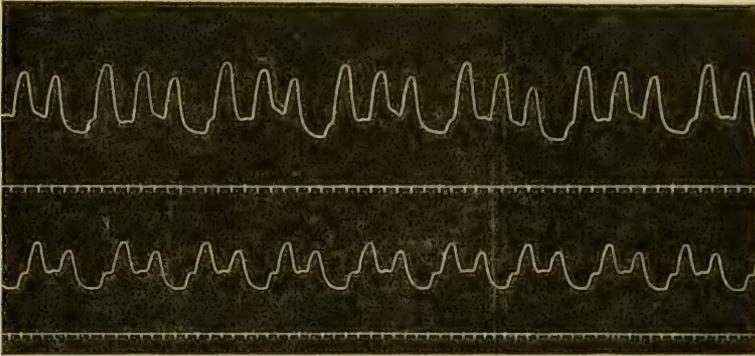


Fig. 8.

increased for the extra-systoles, decreased for the postcompensatory systoles, in comparison with the undisturbed rhythm. The duration of the R-oscillation behaved in the same manner<sup>1)</sup>.

Herewith I suppose, that I have established a law of the conservation of the power of transmission, both for the connecting systems of the separate partitions of the heart and for the heart-muscle itself. In this way LANGENDORFF has established, that the extra-systole is smaller, the postcompensatory systole larger than the normal systoles, and saw in it a law for the conservation of energy for the heart-muscle.

When now, 20 minutes after the reproduction of Fig. 7, I make another reproduction, the basispulsations have ceased and with this again halving of rhythm has taken place, but now with systoles of the point-type. Between every two point-systoles there is now one auricle-systole that is not answered by the ventricle. This second way of halving of rhythm I saw also often in my suspension-curves. As a transition-stage heartpoly-, tri- and bigeminy were formed then.

The slackening of the transmission of stimulation by poisoning with veratrine caused the formation of a split R-top. As an example I give here Fig. 9.

I shall shortly indicate in what manner this electrogram was made.

<sup>1)</sup> The height of the R-top during the extra-systole was enlarged, during the postcompensatory systole diminished. In this manner it was, if the circulation of the blood was undisturbed. That was caused by the bloodfilling of the heart. This was small during the extra-systole, through which the potential differences are less exchanged and stronger during the postcompensatory systole, through which the potential differences are more exchanged. When the bloodcirculation was disturbed all the R-tops had the same height.

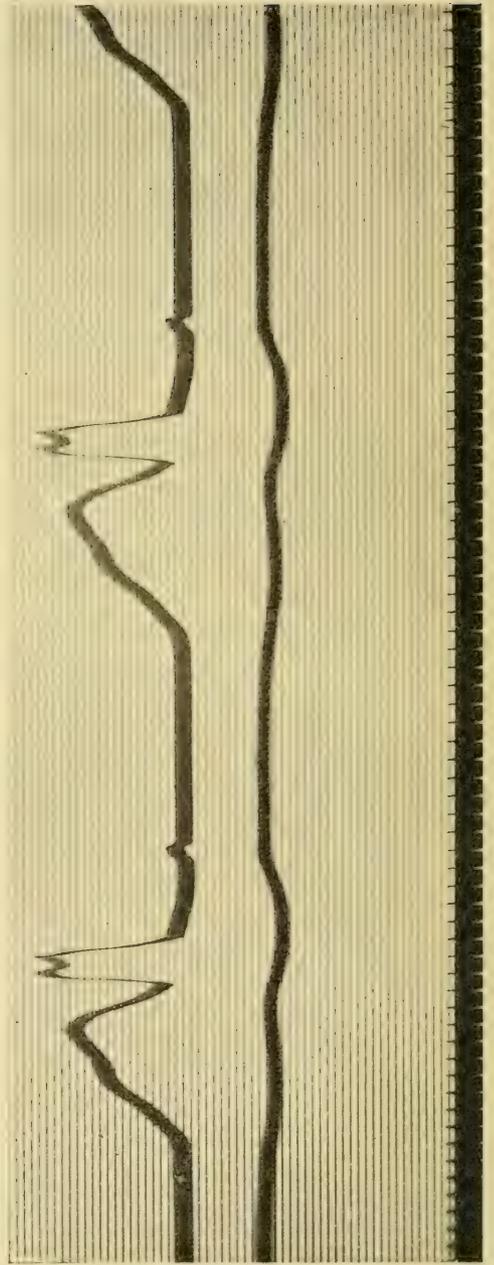


Fig. 9

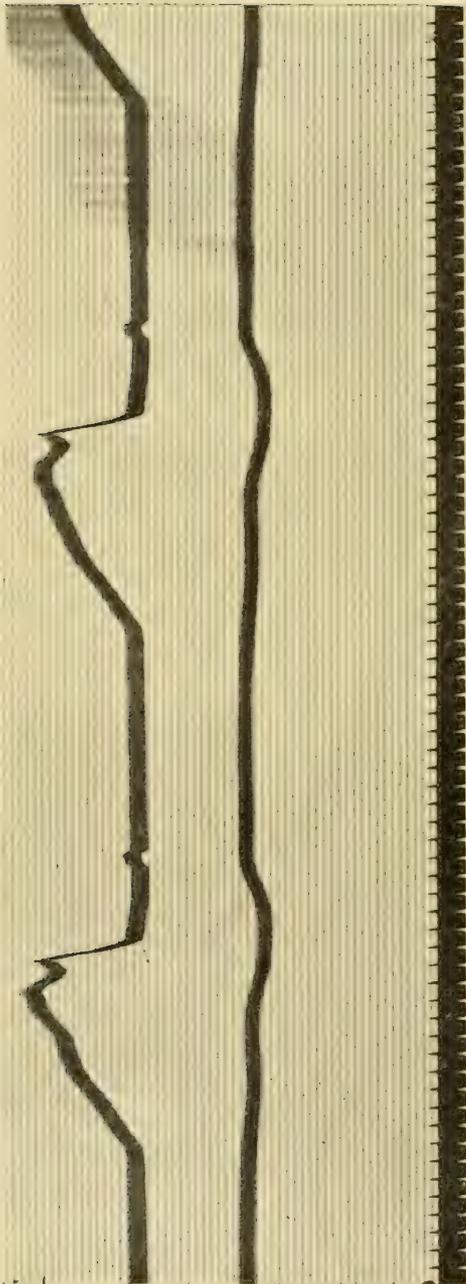


Fig. 10

At half past 2 o'clock I injected the frog 8 drops 1% veratrine into the abdominal cavity; at 10 minutes to three there was halving of rhythm, the electrogram shows a very quick R-top. In the following reproductions at 3 o'clock, 10 min. past, half past 3 and a quarter to four, the R-top remains unsplit, but at every reproduction it becomes wider. The duration of the R-top is in the last reproduction  $1\frac{1}{4}$  time-unity of  $\frac{1}{5}$  second. In the following three reproductions at 5 minutes, 20 minutes, and half past 4 o'clock the duration is  $1\frac{3}{4}$ , 2 and almost 3 time-unities.

With the increase of the duration of the R the splitting becomes more conspicuous after every reproduction. The reproduction of half past four o'clock is represented here in fig. 9. By this the formation of the splitting of the R-branch becomes obvious. By the slackening of the transmission of stimulation the influence of the apexnegativity comes constantly somewhat later (this influence is after all the cause of the decline of R). At last this influence comes so late, that the basisnegativity after the quick original oscillation increases again before the tonical slow oscillation of T.

By the next reproduction, which I made at 4.40, this connection becomes still more conspicuous. For this purpose I had amply cauterized the point of the heart with a red-hot probe. With a, for the rest equal, deduction (auricle-heartpoint) I obtained now the reproduction Fig. 10.

Here I see indeed again the same initial top. This explains the splitting of the top. The cause of it is to be found in the slackening of the transmission of stimulation and the manner in which the heart-muscle contracts.

At the same time we can see in these experiments an experimental proof that the two components, in the interference of which the definitive electrogram originates (at diphasical deduction) consist of a quick initial oscillation and a subsequent slow one. According to SAMOJLOFF, who saw likewise in his monophasical ventricle-curves the initial top, this would originate, because the deduction could never be obtained purely monophasically; he supposed the curves still to be partially diphasical, which would be the origin of the sharp initial top. In my curves, however, the initial top is detected before the influence of the apex-negativity is felt. The part of the ventricle-curve into which the sharp initial top falls is consequently purely monophasical. In the hearts of my frogs that were poisoned with veratrine, I always found this split R-top; it is however no special consequence of the effect of the veratrine, but wheresoever slackening of the transmission of stimulation takes place

the split R-top appears, as likewise with the extra-systoles of mammals.

The latter experiments indicate likewise, how, also with other methods, the splitting of the R-branch can be brought about. For the genesis of the electrocardiogram this fact is of great significance. There is, in my opinion, likewise great probability that the purely diphasical electrogram of the ventricle consists of a quick diphasical R-oscillation, and a T-branch that is either positive or negative. This conception would then at the same time afford an explanation of the formation of the S-branch.

**Zoology.** — "*The physiology of the air-bladder of fishes*". By Dr. K. KUIPER JR. of the Physiological Laboratory at Amsterdam. (Communicated by Prof. MAX WEBER).

(Communicated in the meeting of November 28, 1914).

I. *The air-bladder as a hydrostatic organ.*

For a long time it has been held that fishes possessing an air-bladder could modify its contents by muscular action, which would enable them to regulate, within certain limits their own specific gravity.

If the fish wanted to go down to lower strata a decrease in the contents of its air-bladder would enable it to increase its specific gravity. To rise to the surface it needed only to relax the tension of the muscles of the air-bladder; the gases in the air-bladder expanded and this increased volume carried the fish upward.

In the latter half of the 19<sup>th</sup> century, this view, which was established more especially by BORELLI, and which prevailed during some centuries without being sufficiently tested by experiment, was declared erroneous by A. MOREAU. Some simple but ingenious experiments convinced him that a modification in the S.G. by an active muscular action was out of the question.

A fish which, placed in a cage of thin wire, is submitted to modifications in the pressure on the water in which it is, behaves exactly like the cartesian diver.

He caused a fish to swim round in a glass vessel which was closed hermetically, and which was entirely filled with water. The stopper was pierced by a bent glass tube in which the water-meniscus, when the fish was at the bottom, was found at a certain point, *A* for instance. When the fish swam upward, the meniscus moved slowly forward, that is to say a decrease of the water column

resting upon the fish, increased its volume. When the fish sank to the bottom again the meniscus returned to *A*. Such meniscus-fluctuations did not take place if fishes without air-bladders were put into the vessel. These volume-changes being always synchronous with the vertical movements, MOREAU was led to conclude that they were passive.

According to MOREAU's view, therefore, the fish could not avail itself of its air-bladder to change its S.G. in accordance with the needs of its locomotion. MOREAU, discovered however, in the course of his further experiments that fishes can indeed modify the gas-pressure in the air-bladder. And this happens in such a manner that the fish adapts its S.G. to the water-stratum in which it is. It tries to remain floating in this stratum. If it is placed in deeper water where it is subjected to a greater pressure, the tension of the gases in the bladder increases. The volume which had decreased, owing to the greater pressure from outside, increases again till the S.G. is 1 again in the stratum in which the fish now finds itself.

If the fish is suddenly placed at the surface of the water two things may happen; if the fish is a physostomus, then it lets escape through the ductus pneumaticus, which connects the air-bladder with the esophagus, as much gas as is necessary to bring it in a state of equilibrium in the upper stratum; if the fish is a physoclistus, missing the above-mentioned safetyvalve, then it can get into equilibrium with its new stratum by a slow resorption of the surplus gas. In a natural state, therefore, every fish will, according to MOREAU, have one certain depth where it lives by preference. This plane is called by him "plan des moindres efforts."

Subsequent investigations by CHARBONNEL-SALLE, BAGLIONI and GUYÉNOT strengthened MOREAU's theory. Only JAEGER thinks that BORELLI's view has not been conclusively disproved.

BAGLIONI, who sides with MOREAU, draws the attention to the swimming-movements of a fish when it is exposed to a higher or lower pressure than that to which it is adapted. Besides being a hydrostatic organ the air-bladder is, according to him, an organ of sense which enables the fish to perceive modifications in the pressure.

JAEGER declares himself unconvinced by the experiments of MOREAU and CHARBONNEL-SALLE, and demands that the meniscus-changes of the water in MOREAU's experiment shall correspond exactly with the physical volume-modifications of the air-bladder during the removal to another plane. It is not such a simple thing of course to demonstrate this. JAEGER tries to prove, by the following experiment, that the fish modifies its volume by active muscular

contractions. He repeated MOREAU's second experiment, but took a fish which had been narcotized with ether, and hence sank sideways to the bottom of the glass basin. When the animal came to, it gradually raised itself without any motion of the fins and at the same time the meniscus in the capillary tube moved forward.

GUYÉNOT opposes this view of JAEGER, and tries to prove that both facts and interpretations in JAEGER's study are incorrect.

As it seemed to me that the investigations of both authors showed methodical defects, I resolved to verify them.

It was not difficult to confirm the general phenomena relating to fishes living under modified pressures, as described by MOREAU, BAGLIONI, and others. I could establish that different fishes were sensible to a decreased pressure of from 1—2 centimeters of mercury. Already before this decrease became such as to drive upward a fish resting on the bottom of the basin, it showed by the restless motion of its fins that it responded to this decreased pressure.

I found that in the experiments as carried out by JAEGER and GUYÉNOT, inaccuracies might slip in, which rendered the results absolutely unreliable, inaccuracies which seemed to have been noticed or taken into account by neither of these authors.

The principal mistake was certainly the absence of any means of verifying temperature-changes in the water during the experiment. A large glass bottle into which a bent capillary-tube has been fastened hermetically must needs act as a water-thermometer. If the water in the bottle has not exactly the same temperature as the surroundings, considerable meniscus-movements will be the result, which are by no means due to the presence of the fish in the bottle.

In the preliminary experiments, carried out without a fish, it became obvious that such meniscus-movements resulted indeed from temperature-changes. This rendered the results both of JAEGER and of GUYÉNOT worthless as soon as the experiments of which they were the outcome were of a somewhat longer duration (e.g. a quarter of an hour or longer.)

Hence it was necessary to find a means of eliminating the effect of the temperature.

Therefore the bottle which served as a volumeter was placed in a large water-reservoir, from which the bottle itself was filled. This, however, was found to be no decisive improvement. Changes in the temperature of the room where the experiments were carried out, always brought about a slight change in the temperature of the water. Therefore I placed a second bottle, identical with that used

for the experiment, by the side of the latter. No fish was placed in it. It only served to verify. Before and after the experiment the temperature of the water was taken with a sensitive BECKMANN-thermometer. Thus it could be established whether the changes of the two menisci were due to temperature-fluctuations or not.

My experiments showed that active volume-changes of fishes occur indeed, though in quite another manner than it was supposed by BORELLI and others. Slow meniscus-movements, namely, manifested themselves, which did not run parallel to movements of the fish in the horizontal plane. The meniscus-movements in the bottle could not be explained by expansion of the water as a result of heat-production by the fish, for in all experiments the temperature in the two bottles was the same. What may be the cause of these volume-changes of the fish, which, it must be admitted, are never very great; viz. up to  $\pm 0.3\%$  of its body-volume? Satisfactory explanations might be found in: 1. change of the tonus of the muscles in the surface of the body, 2. changes of pressure in the air-bladder. It seems unlikely that the latter should be the cause. The changes in the gas-pressure found by MOREAU and others, took place very slowly, whilst the volume-changes in my experiments occurred in a rather short time.

A calculation showed that the maximum volume changes, ascertained by me for a fish whose static plane lay at a depth of one metre, caused this plane to move 16 centimetres.

On the ground of the facts mentioned I do not wish to declare myself an adherent of the theory of BORELLI; I only wish to point out that MOREAU'S classical experiments do not sufficiently refute BORELLI'S theory.

We saw already that the fish responds to slight changes in the pressure to which it is subjected namely by well-coordinated swimming-movements. BAGLIONI asked himself where the stimuli arise that awaken these movements, which he looks upon as averting-reflexes. He supposes this to take place in the surface of the air-bladder. The numerous nerve-endings described by DEINEKA would, according to him, be stimulated when the tension in the bladder-surface was modified. In those fishes which possess the well-known organ of WEBER (the 4 pair of bones connecting the surface of the air-bladder with the perilymphatic space of the vestibular apparatus) this organ might be an important factor in the perception of pressure-modifications.

Evidently it is difficult to give direct proofs for the tempting theory of BAGLIONI. It cannot be proved that the upward or down-

ward pressure acting upon the fish, does not cause the swimming-reactions by the stimulation of some other organ such as eye, labyrinth or lateral line.

Some of my experiments lead me indeed to suspect that the pressure modification to which a fish is subjected, is not exclusively perceived by means of the bladder and the organ of WEBER.

MOREAU pointed out that the fish by modifying the gas-density in the bladder can adapt itself slowly to a modification in the pressure. I therefore caused a perch to adapt itself to a decrease of 10 centimetres of mercury. If such a fish is exposed again to normal circumstances, it responds to this pressure, which is now too high for it, by swimming upward. After some time it sinks to the bottom and remains there panting. To the back of the animal a cork was now fastened by means of thin copper-wire, which drew the animal to the surface. On the bladder now presses 1 atmosphere i. e. 10 centimetres of mercury — 25 centimetres of water *more* than that to which the fish adapted itself. Yet the animal continually tries to swim *downward*. Being pulled up by the cork, it remains lying at the surface at last.

This swimming-reaction takes place, therefore, in a direction exactly opposite to that which was caused by the pressure-modification.

That in the ostariophysii the transmission of stimuli is not exclusively due to the organ of WEBER becomes evident from the following fact.

The sensitiveness of tenches to pressure-changes is not affected if, on one or on both sides, the nervus octavus between vestibular-apparatus and brain, is cut through. Since, after the nerve has been cut on both sides, there was no longer any connection between the brain and the static organ, the stimulus must have awakened the swimming-reflex by another route.

Summarized in a few words my conclusions, drawn from the above disquisition, are the following:

1. Active volume-changes can under careful exclusion of disturbing influences, be demonstrated in fishes. Not, however, in the sense in which it is understood by BORELLI's theory. The facts observed by me have been overlooked by MOREAU owing to the short duration of his experiments, by his adherents and opponents owing to technical defects in their experiments.

Cause and significance of the changes have not been discovered yet.

2. In agreement with BAGLIONI we must look upon the air-bladder as a hydrostatic organ of sense.

The stimuli awakened by a modified pressure are certainly perceived via other channels besides that suggested by BAGLIONI.

## II. *The air in the air-bladder.*

Since PRIESTLEY we have known already that the gases, found in the air-bladder, are the same as those of the air. The proportion between oxygen, nitrogen, and carbonic acid varies, however, to a considerable extent. As a rule fishes living in deep water have a high percentage of oxygen; sometimes it rises to  $\pm 90\%$ .

It was established experimentally that the fish is able to gather gases in the interior of its bladder, for example when the gases, present in the first instance, are removed by means of a trocar or air-pump (physostomi).

MOREAU proved that the newly-formed gas is oxygen, at least that after the gas-regeneration the percentage of oxygen is considerably higher than before.

The fish can regulate the gas-pressure in the air-bladder in accordance with the outward pressure to which the fish is subjected. Deep-sea fishes have extremely high tensions in the air-bladder whilst in animals kept under an artificially increased or decreased pressure, an increase or a decrease in the tension of the air-bladder can be demonstrated.

This gas-production cannot be a simple osmotic phenomenon, especially on account of the enormous tension met with in deep-sea fishes; it is a secretion. It is easiest to prove the secretion of oxygen; according to HÜFNER'S investigations, however, we must also assume nitrogen-secretion.

This secretion has especially drawn the attention of BOHR in connection with his researches and hypotheses on the gas-changes in the lungs, which, as we know, are likewise reduced by him to a secretory phenomenon.

BOHR determined which nerves influence the secretion. MOREAU had suggested already that cutting the sympathetic fibres occasioned an increase in the oxygen-percentage. These nerves would, therefore, impede the oxygen-secretion. BOHR cut on both sides the vagus-branches innervating air-bladder and intestines and found that the secretion ceased entirely.

By a series of experiments I tried to fill up to some extent some gaps in our knowledge relating to the secretion-phenomena described above.

Fishes kept under a continually variable pressure adapt themselves

to it by an increased or decreased gas tension. The increase is effected by secretion; the physostomi, which possess a channel from the air-bladder to the esophagus, bring about a decrease by letting one or more gas-bubbles escape, the physoclisti, which lack this safety-valve, by a slow resorption of gases into the blood.

The first question I wanted answered was the following: is it possible to bring about by means of an artificial decrease of the specific gravity of a physoclistus, the same reaction, in the form of gas-resorption from the bladder, as that caused by a decreased outward pressure? For this purpose the time was determined, necessary for perches to adapt themselves to a pressure-decrease of 25 centimetres of mercury. It was found that within 18 hours they had adapted themselves to more than 15 centimetres. Now when by means of corks, fastened to their body, the S. G. of perches was lessened, the same downward swimming-reactions were observed as those occurring at a decreased pressure. The gas-tension in the air-bladder decreased much more slowly. The condition reached in the former experiment within 24 hours manifested itself in the latter category only after about  $5 \times 24$  hours.

Another question that suggested itself was the following: If a fish whose bladder has been emptied, is by means of a cork brought into artificial equilibrium with the surrounding water, will the regeneration of gases no longer take place?

This turns out still to be the case. To a carp the air-bladder of which has been sucked empty, a cork is fastened on the back, of a size to keep the animal in equilibrium in the water. After some days it floats on the surface. The gases have been regenerated again to such an extent that the fish emits air-bubbles when the air-pressure is reduced to less than  $\frac{1}{2}$  atmosphere. It follows from this that the secretion, viewed by MOREAU and others as a reaction on an increased pressure from outside, is independent of the specific gravity of the fish as a whole, but is probably governed by the degree of tension of the bladder.

This tension is but slightly modified by a vertical movement of the fish in the experimental basin (40 centimetres deep), if we compare it with the tension-change in the air-bladder caused by the bladder being sucked empty.

Probably the stimulus causing gas-regeneration finds indeed its origin in the nervous terminal apparatus described by DEINEKA.

As regards the influence of the gas-secretion on the nervous system I may mention that the experiences of BOHR, with reference to the *Gadus callarias* were confirmed by me in the case of *Cyprinus carpio*,

*Tinea vulgaris*, *Perca fluviatilis*. An emptied air-bladder was never filled again after the Rami intestinales Vagi had been cut through on both sides.

Finally I have tried to ascertain if, for some time after the air-bladder has been emptied, an increased absorption of oxygen could be observed. Theoretically there is of course every reason to expect this, and the strong almost asphyxial respiratory movements of the fish after the bladder has been emptied, render it very probable.

The experimental proof is difficult to give. I omit here the technical details relating to the oxygen determinations. On comparing the oxygen consumed by a fish in rest, before the bladder has been emptied and after it, it is found that in the latter case an increase may be observed. It is a remarkable fact, which is difficult to explain, that often immediately after the gas-extraction the oxygen-consumption fell below the average.

**Chemistry.** — “*On critical end-points and the system ethane-naphthalene*”. By DR. ADA PRINS. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of Jan. 30, 1915).

After SMITS' investigation of the system ether-anthraquinone<sup>1)</sup> no other binary system has been found which shows in a similar way the critical end-points. It was, therefore, my intention to search for such a case. Should I succeed in finding end-points  $p$  and  $q$ , which might be easily realized, it would be possible by an appropriate choice of the components to obtain one of the types of ternary systems theoretically developed by SMITS<sup>2)</sup> by combination of two binary ones. As the following shows, I have not been successful in finding a system analogous to ether-anthraquinone; so I had to give up the research of a ternary system.

Obviously either ether or anthraquinone recommended itself as one of the components. As the melting-point of the less volatile component must be above the critical temperature of the more volatile one, and the solubility of the former substance must be slight even at the critical temperature of the latter, and moreover no decomposition may occur, the number of substances suitable for investigation, is not large.

The preliminary experiments, showing whether critical end-points occurred or not, were made in small sealed tubes, which were heated

1) Z. Phys. Chem. 51, page 193.

2) Proc. R. Acad. Amsterdam June 1912.

in an air-bath. If the first critical end-point was observed, the pressure and temperature of  $p$  were determined by the CAILLETET-method and  $q$  was also sought for.

The binary systems which I examined are the following:

*Ether-alizarine.*

A preliminary investigation by SMITS <sup>1)</sup> had already shown that the three-phase line intersects the plaitpoint line. The meltingpoint of alizarine (290°) is about as high as that of anthraquinone (284.6°) and much above the critical point of ether ( $T_k$  193.9°,  $P_k$  36.1 atm.). I observed the first critical end-point  $p$  at 196.4° and 37.5 atm. So the solubility of alizarine in ether proves to be so small, that the critical temperature of ether is only increased by 2.5°. This increment is much smaller than in the case of the ether-anthraquinone system, where  $p$  lies at 203° and 43 atm.

For the determination of  $q$  a mixture of higher concentration of alizarine was required. The large quantity of alizarine caused however the observation to be extremely difficult; the vapour-phase and the liquid-phase were both dark black-red, so that the meniscus was no more to be distinguished. On this account it could only approximately be established, that  $q$  lies about 258°; the system was improper for an exact investigation.

*Ether-hexachlorobenzene.*

The melting-point of hexachlorobenzene lies at 224°; the difference with the critical temperature of ether being much smaller than in the former case. The solubility appeared to be so great, that the three-phase curve does not meet the plaitpoint line.

*Ether-isophtalic acid.*

Isophtalic acid having a high melting-point (330°) dissolves so slightly in ether, that the critical line starting from ether is already intersected at 196.1° and 36.8 atm. Since the isophtalic acid is decomposed by heating a long time at high temperatures,  $q$  could not be determined.

*Hexane-anthraquinone.*

This system does not show critical end-points.

As the combination of either ether or anthraquinone with another

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<sup>1)</sup> Z. Phys. Chem. 51. p. 214.

substance did not give satisfactory results, I resolved to investigate systems one of the components of which is a gas at ordinary temperature.

According to BÜCHNER's research <sup>1)</sup>  $\text{CO}_2$  gives critical end-points with several other substances. It was however not closely examined whether these systems belonged to the simple case ether-anthraquinone or to the type diphenylamine-carbonic acid, discovered by BÜCHNER.

The systems *naphthalene-carbonic acid* and *diphenyl-carbonic acid*, which I studied, showed both the first critical end-point. The fact, that in both systems the three-phase curve starting from the triple point of the solid substance had a steep rise (fig. 1), led to the conclusion, that the systems were analogous to the system diphenylamine-carbonic acid.

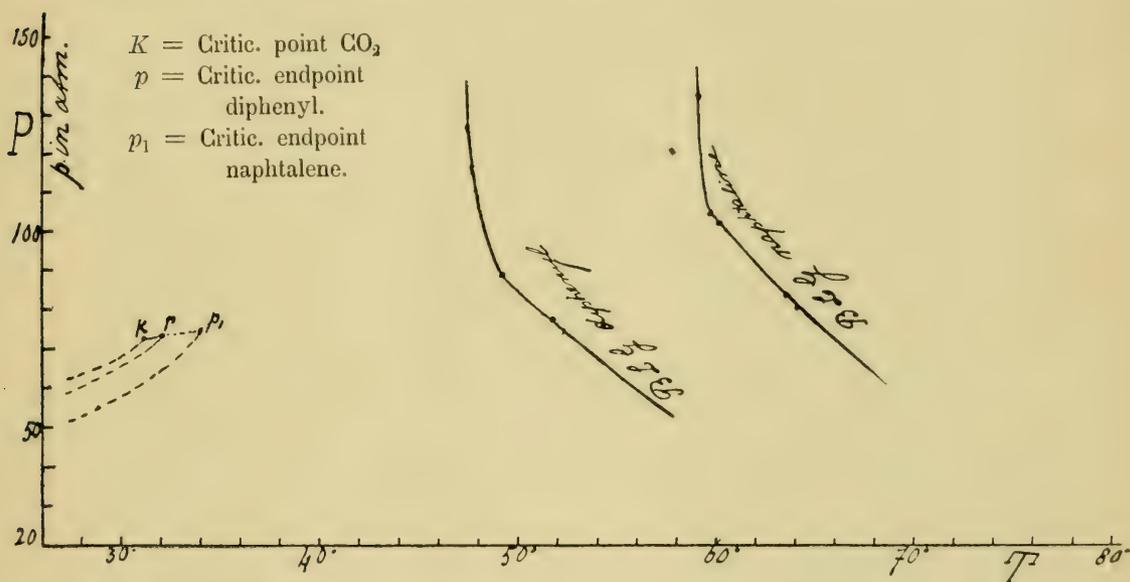


Fig. 1.

This made me suppose that other systems with carbonic acid would also show a steep three-phase curve and accordingly  $q$  at a high pressure or no  $q$  at all. So I resolved to try systems with ethane.

#### *Ethane-naphthalene.*

Preliminary experiments showed also this system to have the above mentioned property. Because it had proved very difficult to find another example of the type ether-anthraquinone and as moreover the phenomena suggested that in this system points might be realized which had not yet been observed, I still commenced a closer study.

<sup>1)</sup> Thesis for the doctorate, Amsterdam 1905.

The type, to which this system belongs has been theoretically developed by BÜCHNER<sup>1)</sup> in his study on systems with limited miscibility, in which together with the equilibrium of fluid phases a solid phase occurs. It has in common with the system ether-anthraquinone, that the melting-point of the less volatile component *B* lies above the critical point of the more volatile *A* and that the solubility of solid *B* in liquid *A* is small. The three-phase curve, on which solid *B* coexists with its solution in liquid *A* and with a vapour-phase, intersects the critical curve starting from the critical point  $L = G$  of the first component, giving rise to the first critical end-point  $p$ . As however the component *B* has not only in the solid state a small solubility in liquid *A*, but also molten *B* is only partially miscible with *A*, the second critical end-point may arise in a way different from that in the system ether-anthraquinone.

From the triple point of *B* a second three-phase curve starts, giving the equilibrium of solid *B* with the solution of *A* in liquid *B* and with a vapour phase. As the melting-point of *B* lies above the critical point of *A* the vapour of this three-phase line at high pressures will have densities corresponding to a liquid; therefore the line will rise steeply. The point of intersection of this curve and the critical line  $L_1 = G$  or  $L_2 = L_1$  is the second critical end-point. Here two liquid phases

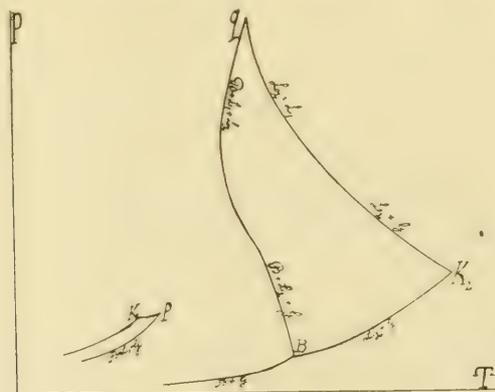


Fig. 2

become identical in presence of a solid phase. Figure 2 represents the  $P$ - $T$  projection of the space figure of this case. BÜCHNER has found the first experimental instance of this type in the system diphenylamine-carbonic acid. The critical end-point  $q$  could not be determined because the critical pressure was not attainable or did not exist.

<sup>1)</sup> loc. cit.

In the system ethane-naphtalene I succeeded not only in finding the point *p*, but also *q*.

The ethane was prepared by electrolyzing sodiumacetate. The anode gas was purified by bromine water and a strong solution of potassium hydroxide, dried over sodalime and condensed in a receiver by liquid air. Subsequently it was again dried over phosphorus pentoxide and separated from the more volatile part by fractionating by the use of liquid air. The disappearance of the discharge in a GEISLER tube attached to the apparatus served as criterion of purity. I determined the critical point from three fractions of the so purified ethane. The following well agreeing values were found:

	$T_k$	$P_k$
1st fraction	31.8°	48.23 atm.
2nd fraction	32.3°	48.09 atm.
3rd fraction	32.35°	48.18 atm.
	} mean 32.32°	} mean 48.13 atm.

The further investigations were made with the second and third fraction.

The naphtalene was purified by sublimation; the melting-point was 80.8°.

The apparatus represented in fig. 3 was used for the preparation of the mixtures.

*A* is the storing-vessel with purified ethane. *B* is calibrated. In *C* ethane may be condensed by liquid air, whereas *D* is filled with cocoanut charcoal to absorb the last traces of air after the evacuation of the apparatus. The Cailletet tube *E* was connected with the rest of the apparatus by rubber tubing protected by mercury. A weighed quantity of naphtalene and an electromagnetic stirrer were placed beforehand in the Cailletet tube and fused on to the top by carefully heating. After exhausting the whole apparatus, the naphtalene being cooled by solid carbonic acid and alcohol, ethane of definite pressure, to be read on the manometer *G*, was pressed over into the Cailletet tube by the aid of air-free mercury contained in the vessel *F*; in this way the required quantity of gas was mixed with the naphtalene. The tube was then placed in the pressure cylinder filled with pure mercury freed from air by boiling. The tube was heated and the pressure regulated in the same way as

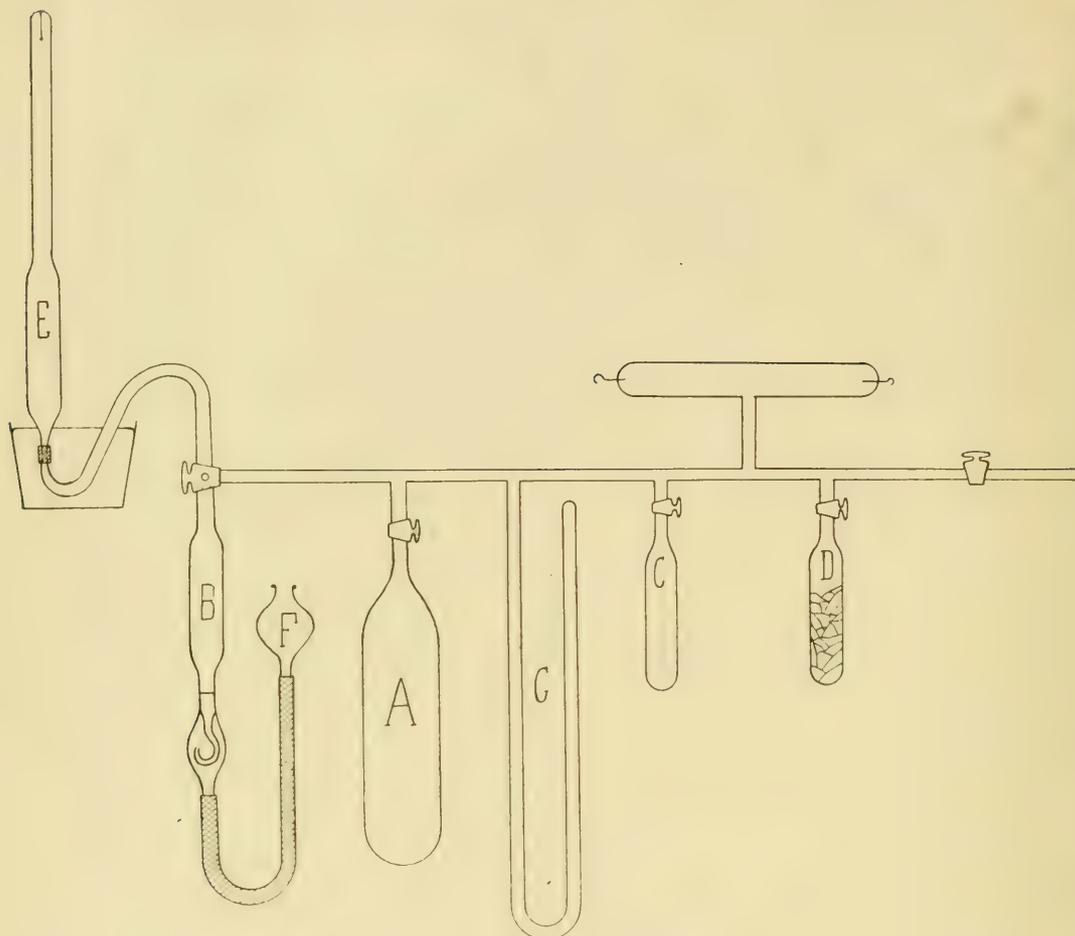


Fig. 3

was already used before in this laboratory.<sup>1)</sup> Fig. 4 shows the  $PT$ -projection of the space figure, whilst table I gives a survey of the observations.

The three-phase line  $BSQ$ , on which solid naphthalene coexists with a solution of ethane in liquid naphthalene and vapour, was determined by slowly heating at a definite pressure till the mass began to fuse. As the equilibria established themselves extraordinarily slowly, the experiments required much time, and it was very difficult to fix the moment that the liquid appeared and increased.

The second critical end-point  $q$  could not directly be observed. It was almost impossible to determine the point, where two phases became identical in the presence of the third, because the temperature varies only extremely slightly at considerable changes of

<sup>1)</sup> SCHEFFER, Proc. Royal Acad. Amsterdam 1912.

TABLE I.

<i>T</i>	<i>P</i> atm.	
32.32	48.13	Critical point ethane.
37.40	51.73	Critical point unsaturated solution
39.40	52.89	<i>p</i>
		Curve <i>BSQ</i>
62.1	47.81	$S_B L_2 G$ of $S_B L_2 L_1$
58.4	59.28	" "
56.3	97.07	" "
55.7	85.96	" "
55.5	78.17	" "
55.1	70.43	" "
		End-condensation line <i>EF</i> , mixture 25 à 26 mol. % napht.
71.4	133.89	$L + G \rightarrow L$
69.3	132.11	"
67.4	130.45	"
65.4	128.68	"
63.5	127.07	"
62.1	125.79	"
59.9	123.76	"
55.7	120.56	" (metastable)
		End-condensation line <i>GH</i> , mixture 24.75 mol. % napht.
66.0	130.26	$L + G \rightarrow L$
62.2	127.57	"
61.05	126.59	"
59.9	125.75	"
57.5	124.06	"
56.5	123.06	" (metastable)
55.05	122.57	" "
52.4	122.27	" "
59.9	126.64	Point max. pressure mixture $\pm 24$ % napht.
55.5	123.81	Point upperbranch <i>PT</i> -loop same mixture.
57.4	124.8	<i>q</i>

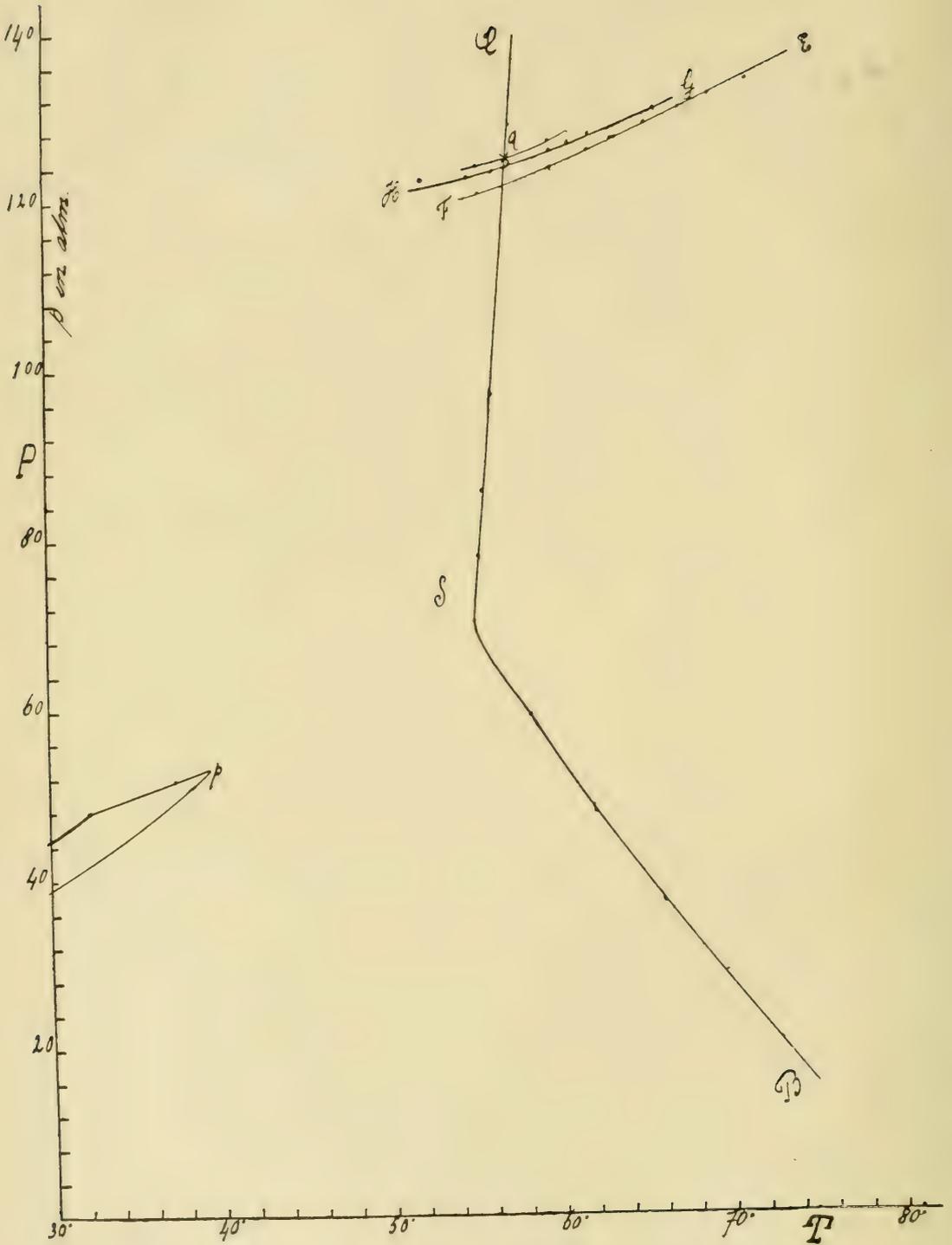


Fig. 4.

the pressure and moreover the appearing and disappearing of the solid is much liable to retardation.

To determine the point  $q$  still as exactly as possible I used the method described below, which offers values, deviating only slightly from the real ones. The following figures will illustrate it.

Fig. 5 gives the  $P$ - $X$  projection of the three-phase line. When we

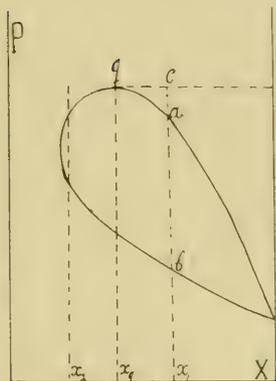


Fig. 5.

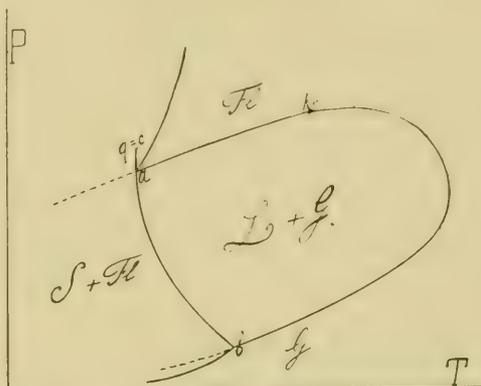


Fig. 6.

consider a mixture of the composition  $x_1$ , which contains more naphthalene than is necessary for realizing  $q$ , we see that the  $PT$  projection of this mixture must be as is drawn in fig. 6, in which the points  $a$ ,  $b$ , and  $c(=q)$  correspond with the homonymous in fig. 5. This section gives the part of the three-phase line between  $b$  and  $c(=q)$ . If a direct determination had been possible,  $q$  might have been found with this mixture. Although I failed to find  $q$ , I could study in this section the line of end-condensations, and the point of intersection  $a$  of this curve with the three-phase line (see table I and fig. 4).

This point  $a$  will slightly differ from  $q$ , when  $x_1$  lies near  $x_q$ . From the distance of  $kr(L=G)$  from  $a$  we can judge whether this is actually the case, because in the  $PT$  section  $x_q kr$  and  $a$  coincide. The smaller the distance the nearer we are to  $q$ . It is however possible that the composition along the critical line varies only slightly with the temperature, so that in a mixture the composition of which differs slightly from  $x_q kr$  is nevertheless far from  $a$ . This proved to be actually the case on studying a second mixture. If the concentration of this mixture had been exactly that of  $q$ , then the  $PT$  projection of fig. 7 would have been found. Here the point  $q$  lies just on the line of the end-condensations. By studying the upper branch of the loop-line  $LG$ , on which the meniscus dis-

appears at the bottom and determining graphically the point of intersection with the three-phase line,  $q$  might be found.

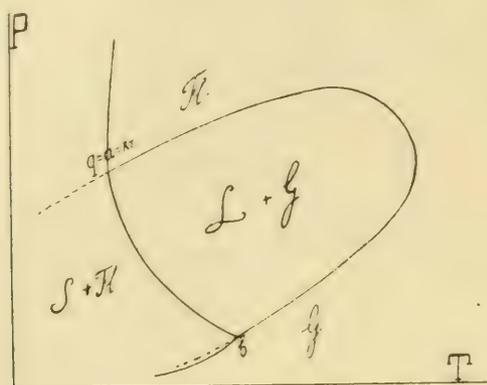


Fig. 7.

Fig. 8 gives the  $P$ - $T$  projection for a mixture  $x_2$ , which has a concentration smaller than  $x_q$ . The point  $kr$  has entered the meta-stable region, so that the upper limit of the  $L$ - $G$  region here also

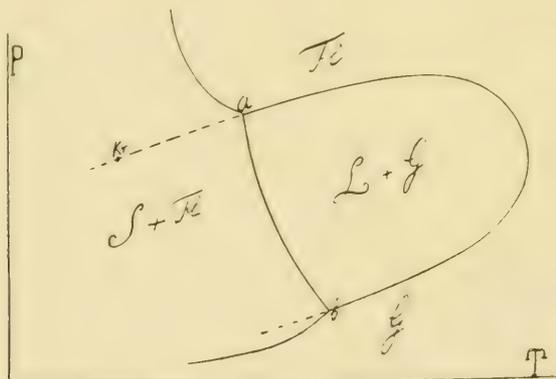


Fig. 8.

is indicated by the disappearance of the meniscus at the bottom. Here the point  $kr$  can only be realized, when the solid phase does not appear. The stable part of the  $L$ - $G$  loop must offer everywhere retrograde phenomena. If the composition on the critical line varies only slightly when the temperature rises, the point  $kr$  in fig. 8 also will move rapidly from  $a$  to lower temperatures, when  $x_2$  differs slightly from  $x_q$ . The point  $q$  is never to be realized with a mixture  $x_2 < x_q$ , though here as well  $a$  will deviate slightly from  $q$  when the difference between  $x_2$  and  $x_q$  is small.

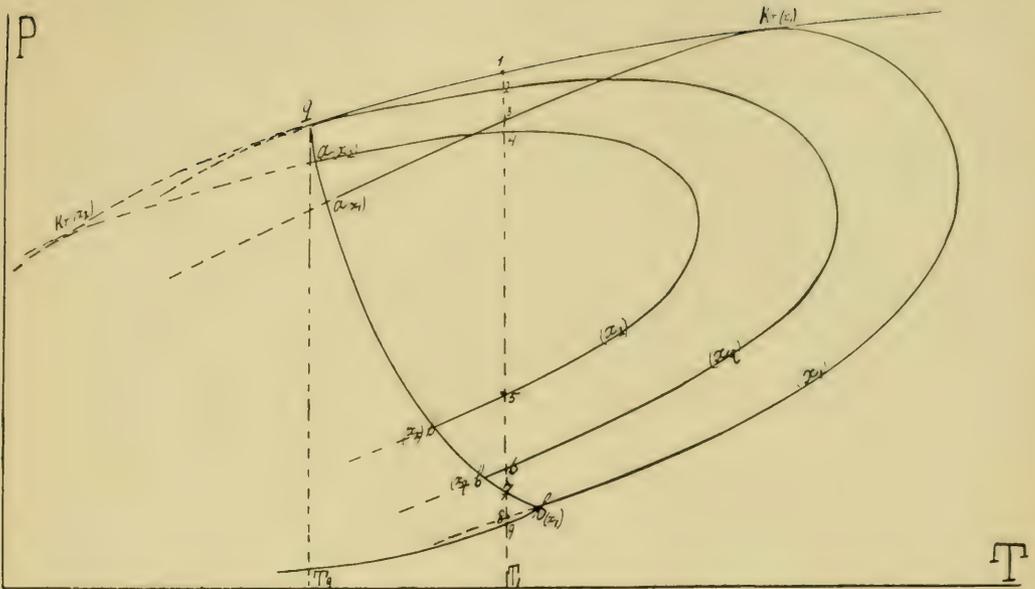


Fig. 9.

The combination of the fig. 6, 7, and 8 gives fig. 9. When we draw the  $P$ - $X$  section for  $T_1$  we obtain fig. 10, where the points corresponding with those in fig. 9 are denoted by the same numbers.

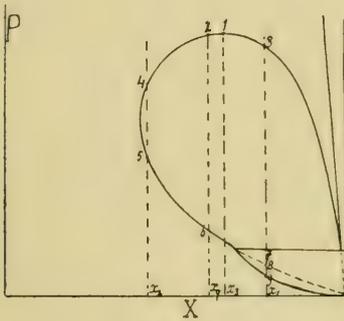


Fig. 10.

this is still more exactly the case when the composition of the critical line varies little with variation of the temperature. To find the composition of 1 experimentally we must start from a mixture  $x_1$ , which contains more solid substance than is required for  $q$ . With this mixture we determine at  $T_1$  the point of end-condensation 3. Then after cooling some of the solid substance is pushed under the mercury meniscus, whereby the composition of the mixture is changed a little to the left in fig. 10. Again with the composition so obtained e.g.  $x_2$  we determine the upper limit of the loop  $LG$  at  $T_1$ . When we isolate successively different quantities of the solid, points of the line 3, 1, 2 and 4 in the  $P$ - $X$  section may be found. Evidently the maximum pressure, point 1, corresponds to the mixture  $x_2$ . If therefore the maximum pressure is realized, we have the mixture  $x_3$ , deviating a little from  $x_q$ , at least if  $T_1$  deviates slightly from  $T_q$ .

So when with this mixture the upper limit of the  $P$ - $T$  loop is determined, the intersection of this curve with the three-phase line will give approximately the point  $q$ .

The first mixture, that I studied, corresponds to  $x$ , in fig. 5. Determining the upper limit of the  $P$ - $T$  loop, I saw the meniscus always disappear in the top of the tube, so that  $kr$  must lie at a temperature higher than  $71.4^\circ$ . (see fig. 6, fig. 2 line  $EF$  and table I). The composition of this mixture was between 25 and 26 mol. % naphthalene. As I did not succeed in observing  $q$  directly with this mixture, although I sometimes saw a fluid phase in contact with solid, I resolved to proceed along the previously described way.

The second mixture contained 24.75 mol. % naphthalene; it might therefore lie on the left or on the right of  $q$ , or it might happen to have exactly the composition of  $x_q$  itself.

On determining the  $P$ - $T$  loop the meniscus also here always disappeared in the top of the tube, indicating, that the mixture contained more naphthalene than  $x_q$  (see table 1 and fig. 2 line  $GH$ ). Three points could be found on the metastable part of the curve. The pressure of the point at  $52.4^\circ$  and 122.27 atm. is high, which can be explained by assuming that perhaps some solid has got under the mercury.

With this mixture the composition of point 1 from fig. 10 was experimentally sought. From the intersection of the two end-condensation lines with the three-phase curve I might conclude, that  $q$  lay at about  $57^\circ$ . I chose  $59.9^\circ$  as temperature of the experiment, also  $2.9^\circ$  higher than the assumed  $T'_q$ . The above mentioned method gave at  $59.9^\circ$  a pressure maximum of 126.64 atm.

With this mixture, showing  $kr$  at  $59.9^\circ$  and 126.64 atm. another point of the  $PT$  loop was determined at a temperature lower than  $kr$ . The meniscus disappeared a little below the middle of the tube at  $55.5^\circ$  and 123.81 atm. (metastable point). The intersection of the curve, which joins those two points, with the three-phase curve offers a value for  $q$ , which is very near the true one. This shows the second critical end-point to lie at  $57.4^\circ$  and 124.8 atm. and the composition to be between 20 and 25 mol. %.

Finally I wish to express my thanks to Dr. F. E. C. SCHEFFER for his help and advice.

*Amsterdam, January 1915.*

*Inorg. Chem. Laboratory  
of the University.*

**Mathematics.** — “*Systems of circles determined by a pencil of conics*”. By PROFESSOR JAN DE VRIES.

(Communicated in the meeting of Jan. 30, 1915.)

The osculating circles and the bitangent circles of the conics of a pencil form two doubly infinite systems: of these I shall consider some properties in this paper.

1. Any straight line  $n$  passing through a base-point  $B$  of a pencil of conics ( $\beta^2$ ), is a normal line of *one*  $\beta^2$ . To  $n$  I associate the diameter  $m$  of  $\beta^2$  passing through  $B$ . As each line passing through  $B$  bears the centre of two  $\beta^2$ , a correspondence (2,1) exists between  $m$  and  $n$ . Each coincidence is an axis; *each base-point is therefore vertex of three conics: the axes envelop a curve of class three,  ${}^3a$ .*

As the line at infinity  $l_\infty$  is axis for the two parabolae of the pencil, consequently *bitangent* of  ${}^3a$ , only *one* axis belongs to a pencil of parallel rays.

The axes  $a$  form on the rational curve  ${}^3a$  a quadratic involution, of which each pair consists of the axes  $a_1, a_2$  of a definite conic. The *central conic* of the pencil (locus of the centres) is the curve of involution and at the same time part of the *orthoptic line* of  ${}^3a$ ; the missing part<sup>1)</sup> is apparently the line  $l_\infty$ .

The locus of the vertices  $T$  of the conics  $\beta^2$  has a triple point in each base-point. As an arbitrary  $\beta^2$  has four vertices, it will have 16 points in common with  $(T)$ ; the curve in question is therefore of order 8. It has apparently nodes in the nodes  $D$  of the degenerated conics. *The vertices of the conics lie therefore on a  $(T)^8$  with four triple points and three nodes.*

2. Each  $\beta^2$  possesses two systems of *bitangent circles*,  $\gamma_{2,2}$ . For the parabolae *one* system exists of the pairs of lines formed by a tangent and the line  $l_\infty$ .

As each point  $P$  bears three axes,  $P$  is the centre of three circles  $\gamma_{2,2}$ . A perpendicular to the plane  $\tau$  of ( $\beta^2$ ) contains therefore six poles of circles  $\gamma_{2,2}$ , in other words the system  $[\gamma_{2,2}]$  is the cyclographic representation of a surface of order six,  $\omega^6$ .

The intersection of  $\omega^6$  with  $\tau$  is apparently the locus of the foci (*focal curve of the pencil*); the latter is consequently a bicircular curve of order six, having the nodes of the three pairs of lines as nodes.

The tangents  $p$  of the two parabolae are the images of the points at infinity on the cones of revolution  $\omega^2$ , the generatrices of which

<sup>1)</sup> On a straight line  $r$ , the pairs of orthogonal tangents of  ${}^3a$  determine a (3,3). Any intersection of two orthogonal tangents is a double coincidence; the orthoptic line is therefore a figure of order 3.

intersect the plane  $\tau$  at angles of  $45^\circ$ . As two tangents  $p$  may be drawn in any direction, the curve at infinity  $\sigma_x^2$  of those cones is nodal curve of  $\omega^6$ .

The circles passing through two points  $P, Q$  are the images of an orthogonal hyperbola  $\mu^2$ , situated in the normal plane in the middle of  $PQ$ , with the middle of  $PQ$  as centre, while its asymptotes intersect  $\tau$  at angles of  $45^\circ$ .

As it has four points in common with  $\sigma_x^2$  it intersects  $\omega^6$  in eight finite points, which will be the poles of four circles  $\gamma_{2,2}$  passing through  $P, Q$ . *Through two arbitrary points pass therefore four bitangent circles.*

If one of these points is a point at infinity, each of the four circles is formed by  $l_x$  with one of the tangents going from the other point to the two parabolae<sup>1)</sup>.

3. The circles  $\gamma_{2,2}$  passing through a point  $P$  form the image of the intersection of  $\omega^6$  with the cone of revolution  $\omega^2$ , having  $P$  as vertex, while its edges intersect  $\tau$  at angles of  $45^\circ$ . The latter has in common with  $\omega^6$ , besides the nodal curve  $\sigma_x^2$ , also a  $\varrho^8$ , containing the poles of the circles  $\gamma_{2,2}$  passing through  $P$ . Hence: *the locus of the centres of the bitangent circles passing through a fixed point is a curve of order four,  $p^4$ .*

The tangents from  $P$  to the two parabolae determine the points at infinity of this curve. It is intersected by the perpendicular at the middle point of  $PQ$  in the centres of the  $\gamma_{2,2}$  passing through  $P$  and  $Q$ .

Let us consider the corresponding locus for the case that  $P$  is replaced by a base-point  $B$ . Any ray  $n$  passing through  $B$  is normal line of one  $\beta^2$ , consequently contains the centres of two  $\gamma_{2,2}$  touching this  $\beta^2$  in  $B$ ;  $B$  cannot be centre of such a circle; so the locus in question is a conic. This was to be expected, for the four tangents of the parabolae determining the centres at infinity coincide here in pairs. The central curve  $p^4$  will have the perpendicular in the middle of  $PB$  as bitangent.

4. The circles having the axes of  $\beta^2$  as diameters belong to the system  $[\gamma_{2,2}]$ . These *principal circles* are represented on  $\omega^6$  by a twisted curve  $\varrho^8$ , having the central conic of ( $\beta^2$ ) as projection. For any point of the centre is centre of two principal circles so that

<sup>1)</sup> Similar considerations concerning the system of the orthoptic circles of ( $\beta^2$ ) may be found in my paper "On the orthoptic circles belonging to linear systems of conics" (These Proceedings I, 305—310).

any plane perpendicular on  $\tau$  contains eight poles.  $\varrho^8$  is four times intersected on  $\sigma_\infty^2$  by the cone of revolution  $\omega^2$  (§ 3); the remaining intersections are poles of six principal circles. *The principal circles form therefore a system with index six.*

As a base-point  $B$  is vertex of three  $\beta^2$ , consequently lies on three principal circles, these circles are to be counted twice.

5. We shall now consider the system formed by the *osculating circles*,  $\gamma_3$ , of the conics of the pencil. For a point  $R_\infty$  of  $l_\infty$ ,  $\gamma_3$  consists of  $l_\infty$  and the asymptote touching in  $R_\infty$ . To the osculating circles of the two parabolae belong the figures consisting of  $l_\infty$  and a diameter.

*The asymptotes envelop a curve of class three,  ${}^3\beta$ , which has  $l_\infty$  as bitangent. The tangents of  ${}^3\beta$  passing through a base-point  $B$  are apparently the lines connecting  $B$  with the other three base-points.*

The circles  $\gamma_3$  passing through a point  $P$  and a point  $Q_\infty$  consist of  $l_\infty$  combined with an asymptote or a diameter of a parabola; their number amounts therefore to *five*.

From this it may be deduced that through any two points  $P, Q$ , five osculating circles may be laid.

First it may be observed that *the locus of the centres of the circles  $\gamma_3$  passing through  $P$  must be a curve  $c^5$ , for five of those circles have their centre on  $l_\infty$ .*

If the system  $[\gamma_3]$  is considered as the cyclographic representation of a surface  $\Omega$ ,  $c^5$  is the orthogonal projection of a curve  $\varrho^{10}$  lying on  $\Omega$ . The latter has 20 points in common with the orthogonal hyperbola  $\mu^2$  (§ 2) determined by  $P$  and  $Q$ . Of these 10 lie on the curve  $\sigma_\infty^2$  (§ 2) representing the asymptotes; the remaining 10 form 5 pairs of poles of circles passing through  $P$  and  $Q$ . *Consequently five circles  $\gamma_3$  pass through two given points.*

The cone of revolution  $\omega^2$  (§ 3) with vertex  $P$  has in common with  $\Omega$  the curves  $\sigma_\infty^2$  and  $\varrho^{10}$ ; so  $\Omega$  is a surface of order six. Hence, *any point of the plane  $\tau$  is centre of three osculating circles.*

6. Let  $S$  be the intersection of a  $\beta^2$  with the osculating circle which has  $B$  as point of contact,  $u$  a ray passing through  $B$  parallel to one of the axes of  $\beta^2$ . In order to investigate how often a straight line  $k$  drawn through  $B$  becomes chord of osculation, we associate the reflected image  $s$  of  $k$  with regard to  $u$  to the straight line  $t$ , touching  $\beta^2$  in  $B$ . To a line  $t$  belong two lines  $u$ , but only *one* line  $s$ ; a ray  $s$  determines with  $k$  two lines  $u$ , but only *one*  $\beta^2$ , consequently *one* ray  $t$ . The two coincidences  $s \equiv t$  belong to two

conics having  $k$  as chord of osculation  $BS$ . As  $B$  is vertex of three  $\beta^2$ , consequently coincides thrice with  $S$ , the locus of  $S$  will be a curve  $\sigma^5$ , having a triple point in  $B$  and nodes in the remaining base-points. It passes moreover through the cyclic points  $I, J$ , on  $l_\infty$ , for on the  $\beta^2$  laid through  $I$  that point  $S$  belongs to all circles of osculation.

We can now easily point out the five circles  $\gamma_3$  passing through two base-points  $B_1, B_2$ : two osculate in  $B_1$  and intersect in  $B_2$ , two osculate in  $B_2$  and intersect in  $B_1$ , the fifth consists of  $B_1B_2$  and  $l_\infty$ .

That *any* line  $l$  is chord of osculation for five circles  $\gamma_3$  may be proved as follows.

If in each point  $L$  of  $l$  the tangent  $t$  is drawn at the  $\beta^2$  passing through  $L$ , a system of rays with index 3 is obtained; for  $l$  is touched by two  $\beta^2$ , is consequently bitangent of the curve enveloped by  $t$ . Through  $L$  we draw the lines  $u$  and  $u'$  parallel to the axes of  $\beta^2$  and the lines  $v$  and  $v'$ , bisecting the angles between  $l$  and  $t$ . If the pair of lines  $v, v'$  coincides with  $u, u'$ ,  $l$  is chord of osculation of  $\beta^2$ .

If  $t, u, u', v, v'$ , retaining their directions, are transferred to a point  $O$  of  $l$ , a correspondence (4,6) arises in the pencil of rays ( $O$ ). For a ray  $u$  determines (§ 1) *one*  $\beta^2$ , so two points  $L$  and four rays  $v$ ; a ray  $v$  determines three tangents  $t$ , therefore six rays  $u$ . The ten coincidences  $u \equiv v$  form five orthogonal pairs; so there are *five conics for which  $l$  is chord of osculation*.

If the point of contact  $L$  of a  $\gamma_3$  describes the straight line  $l$ , the end  $S$  of the chord of osculation will describe a curve of order thirteen, for on  $l$  lie eight vertices of conics.

**7.** On each conic  $\beta^2$  arises a cubic involution, if the three points  $R$ , of which the osculating circles meet in a point  $S$  of  $\beta^2$ , are joined into a group.

If  $\beta^2$  is an hyperbola, this  $I_3$  has the points of contact of the asymptotes as triple elements; these two replace the four groups with a two-fold element, which an  $I_3$  possesses in general.

For the ellipse these triple elements become imaginary; for if it is considered as the orthogonal projection of a circle, the  $I_3$  appears to be the projection of the  $I_3$  formed by the angular points of the regular triangles described in that circle.

For a parabola each group of the  $I_3$  consists of a point of the parabola and the point at infinity of that curve counted twice.

Let us now consider the *triple involution*  $T_3$ , in the plane  $\tau$ ,

formed by the involutions  $(R_1, R_2, R_3)$  belonging to the conics of the pencil  $(\beta^2)$ .

The curves  $\sigma^5$  belonging to two base-points  $B_1, B_2$  (§ 6) have in those points 12 intersections and 8 in  $B_3, B_4$ ; they further pass through the cyclic points on  $l_\infty$  and through the point at infinity of  $B_3, B_4$ . The two points  $S$ , which they have moreover in common are each the end of two chords of osculation  $B_1S, B_2S$ . Any two base-points belong therefore to two groups of  $T_3$ .

Let us now consider the locus of the points  $R_2, R_3$  belonging to  $R_1 \equiv B_1$ . This singular curve,  $\beta_1$ , has nodes in  $B_2, B_3, B_4$ , but does not pass through  $B_1, T_3$  possessing no coincidences outside  $l_\infty$ . As an arbitrary conic of  $(\beta^2)$  contains *one* pair  $R_2, R_3$ , consequently has eight points in common with  $\beta_1$ , *each base-point determines a rational singular curve of order four*.

The *parabola*e too are *singular curves* and as such associated to their points at infinity.

Any straight line  $B_k B_l$  corresponds to itself in the transformation  $(R_1, R_2)$ ; for each of its points may be considered as point of contact of a  $\gamma_3$ , intersecting  $B_m B_n$  on  $l_\infty$ .

If  $R_1$  describes a  $\beta^2$ ,  $\beta^2$  is described twice by  $R_2 (R_3)$ . So  $\beta^2$  is transformed by  $(R_1, R_2)$  into the figure composed of the four singular curves  $\beta_k^4$  and the conic  $\beta^2$  counted twice, consequently into a figure of order 20. From this it ensues that *the transformation in question transforms a straight line into a curve of order ten*.

This  $c^{10}$  has in each base-point a *quadruple point*.

**Chemistry.** — “*Compounds of the arsenious oxide*”. I. By Prof. F. A. H. SCHREINEMAKERS and Miss W. C. DE BAAT.

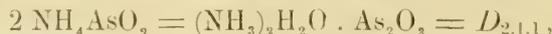
*The system:  $H_2O-As_2O_3-NH_3$  at  $30^\circ$ .*

Of the different ammonium arsenites which may be imagined to be deduced of the  $H_3AsO_3$ ,  $H_4As_2O_5$  and  $HAsO_2$ ,  $(NH_4)_4As_2O_5$  and  $NH_4AsO_2$  are described as crystals and  $(NH_4)_3AsO_3$  as a thick-fluid yellow mass.

Now we have examined the system  $H_2O-As_2O_3-NH_3$  at  $30^\circ$ ; from this it is apparent that the salt  $NH_4AsO_2$  occurs at  $30^\circ$ , while the possibility that also still a salt of the composition  $NH_4H_2AsO_3$  exists, is not excluded.

In fig. 1 we find a schematical representation of the equilibria occurring in this system at  $30^\circ$ ; with the aid of table I we can accurately draw the different curves.

The point  $D_{2.1.1}$  represents the  $\text{NH}_4\text{AsO}_2$ ; in order to find the position of this point in the triangle, we must consider that:



the salt  $\text{NH}_4\text{AsO}_2$  contains consequently 13.6%  $\text{NH}_3$ , 7.2%  $\text{H}_2\text{O}$  and 79.2%  $\text{As}_2\text{O}_3$  so that the position of the point  $D_{2.1.1}$  is known.

The point  $D_{2.3.1}$  represents the  $\text{NH}_4\text{H}_2\text{AsO}_3$ ; as



this salt contains 11.9%  $\text{NH}_3$ , 18.9%  $\text{H}_2\text{O}$  and 69.2%  $\text{As}_2\text{O}_3$ .

When we draw in the figure the points  $D_{2.1.1}$  and  $D_{2.3.1}$ , then it is apparent that they are situated on a straight line with the angle-point  $W$ . That this must really be the case, follows also from the equation



from which it is apparent that the  $\text{NH}_4\text{H}_2\text{AsO}_3$  may be considered as consisting of  $\text{NH}_4\text{AsO}_2$  and  $\text{H}_2\text{O}$ .

Curve  $ab$  represents the solutions saturated with solid  $\text{As}_2\text{O}_3$ ; these complexes have been shaken during about a month at  $30^\circ$ . The  $\text{As}_2\text{O}_3$  which we have used was an extremely fine flour-like powder; in each of the small bottles we brought a little sublimated  $\text{As}_2\text{O}_3$  and a little  $\text{As}_2\text{O}_3$  which was recrystallized from a strong, heat solution of chloric acid.

Point  $a$  represents the solubility of  $\text{As}_2\text{O}_3$  in pure water; as it is apparent from table I we find for this 2.26%; BRUNER and TOLLOZKO found that at  $25^\circ$  and  $39.8^\circ$  in 100 Gr. water 2.03 and 2.93 Gr.  $\text{As}_2\text{O}_3$  are dissolved. It appears from the analysis of the rests that the solid phase is not a hydrate, but that it is the anhydric  $\text{As}_2\text{O}_3$ .

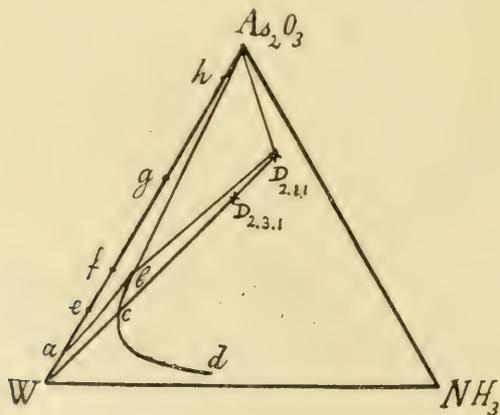


Fig. 1.

Curve  $bed$  represents the solutions with  $D_{2.1.1} = \text{NH}_4\text{AsO}_2$ . As the

line  $W.D_{2.1.1}$  intersects this curve  $bd$  in the point  $c$ , the salt  $\text{NH}_4\text{AsO}_2$  is soluble in water at  $30^\circ$  without decomposition. The saturated aqueous solution of this salt is represented by point  $c$ ; it is apparent from the position of the points  $W$ ,  $c$  and  $D_{2.1.1}$  with respect to one another that this solution contains  $\pm 19.2\%$   $\text{NH}_4\text{AsO}_2$ .

We have deduced with the aid of the rest-method the composition of the solid phase, which is in equilibrium with the solutions of branch  $bcd$ . The conjugationlines liquid-rest are going viz. all through the point  $D_{2.1.1}$ . As the point  $D_{2.3.1}$ , however, is situated close to  $D_{2.1.1}$ , the conjugationlines for the solutions of branch  $bc$  go within the errors of analysis, also through the point  $D_{2.3.1}$ . Although it is, therefore, sure that the solutions of  $cd$  which are situated at some distance of  $c$ , are saturated with  $D_{2.1.1} = \text{NH}_4\text{AsO}_2$ , yet the possibility exists that the other solutions are saturated with  $D_{2.3.1} = \text{NH}_4\text{H}_2\text{AsO}_3$ .

It is apparent from the table that branch  $bcd$  is determined no further than to a solution  $d$ , which contains  $14.28\%$   $\text{NH}_3$ . In order to examine if with higher content of  $\text{NH}_3$  in the solution perhaps still a compound should occur with more  $\text{NH}_3$  than in the compound  $\text{NH}_4\text{AsO}_2$ , we have still examined a solution at  $0^\circ$ , which contained  $36.05\%$   $\text{NH}_3$ . It was apparent that also in this case the solid phase was still the  $\text{NH}_4\text{AsO}_2$ .

From the course of curve  $ab$  and from table 1 it is apparent that the solubility of the  $\text{As}_2\text{O}_3$  increases strongly with increasing content of ammonia of the solution. The terminating point  $b$ , viz. the solution which is saturated with  $\text{As}_2\text{O}_3 + \text{NH}_4\text{AsO}_2$ , is not determined. The solution of branch  $ab$  which is experimentally determined and which is situated the nearest to the point  $b$  contains (compare table)  $21.17\%$   $\text{As}_2\text{O}_3$  and  $2.86\%$   $\text{NH}_3$ . It is apparent from the course of the branches  $ab$  and  $bcd$  that the solution  $b$  will contain  $\pm 22\%$   $\text{As}_2\text{O}_3$  and  $\pm 2.87\%$   $\text{NH}_3$ . From this it appears, therefore, that small quantities of  $\text{NH}_3$  strongly increase the solubility of the  $\text{As}_2\text{O}_3$ .

We imagine in fig. 1 the line  $\text{NH}_3-b$  to be drawn; its point of intersection with the side  $W-\text{As}_2\text{O}_3$  is represented in the figure by  $f$ ; this point  $f$  indicates a complex which contains  $\pm 22.5\%$   $\text{As}_2\text{O}_3$  and consequently  $\pm 77.5\%$  water. Now we take a complex  $e$ , situated between  $a$  and  $f$ ; this contains, therefore, more than  $2.26\%$  and less than  $22.5\%$   $\text{As}_2\text{O}_3$  and consequently it consists of solution  $a +$  solid  $\text{As}_2\text{O}_3$ . When we bring  $\text{NH}_3$ -gas into this complex, then it follows the line  $e-\text{NH}_3$ ; this line intersects, starting from  $e$ , firstly the region  $ab \text{ As}_2\text{O}_3$ , afterwards the region  $Wabcd$  and further the region  $bcd.D_{2.1.1}$ . Hence it follows that by adding

gaseous  $\text{NH}_3$  first the  $\text{As}_2\text{O}_3$  is dissolved and an unsaturated solution occurs and that on further addition of  $\text{NH}_3$ , the solid  $\text{NH}_4\text{AsO}_2$  is separated; the solution follows the curve  $bcd$  in this case, starting from  $b$  and gets, therefore, gradually poorer in  $\text{As}_2\text{O}_3$ , which is deposited as  $\text{NH}_4\text{AsO}_2$ . We imagine also in fig. 1 the line  $\text{NH}_3 - D_{2.1.1}$  to be drawn; its point of intersection with  $W - \text{As}_2\text{O}_3$  is represented by  $h$ . The point  $h$  indicates a complex which contains  $\pm 91.5\%$   $\text{As}_2\text{O}_3$  and consequently  $\pm 8.5\%$  water. Now we take a complex  $g$  between  $h$  and  $f$ ; this contains, therefore, more than  $22.5\%$  and less than  $91.5\%$   $\text{As}_2\text{O}_3$  and it consists of solution  $a +$  solid  $\text{As}_2\text{O}_3$ . When we bring  $\text{NH}_3$ -gas into this complex, it follows the line  $g - \text{NH}_3$ ; this line intersects, starting from  $g$ , first the region  $ab \text{As}_2\text{O}_3$ , after that the threephasetriangle  $b \cdot D_{2.1.1} \cdot \text{As}_2\text{O}_3$  and afterwards the region  $bcd \cdot \text{As}_2\text{O}_3$ . Hence it follows that on addition of gaseous  $\text{NH}_3$  first  $\text{As}_2\text{O}_3$  is dissolved until solution  $b$

TABLE I.

Compositions in percentages by weight at  $30^\circ$ .

of the solution		of the rest		solid phase
$\%$ $\text{NH}_3$	$\%$ $\text{As}_2\text{O}_3$	$\%$ $\text{NH}_3$	$\%$ $\text{As}_2\text{O}_3$	
0	2.26	—	—	$\text{As}_2\text{O}_3$
1.41	10.98	0.37	59.79	"
2.78	20.49	1.24	63.10	"
2.86	21.17	1.21	64.26	"
2.88	18.43	7.43	43.13	$\text{NH}_4\text{AsO}_2$
3.13	12.30	7.25	38.59	"
3.18	11.13	7.51	38.39	"
3.91	7.63	8.24	35.80	"
5.82	5.61	9.08	36.44	"
6.95	4.72	9.74	35.55	"
9.25	3.44	11.42	41.79	"
9.93	3.20	11.74	42.44	"
10.06	3.14	12.22	49.14	"
13.98	2.50	13.78	42.50	"
14.28	2.16	13.77	44.78	"

is formed; the liquid contains then 22 %  $\text{As}_2\text{O}_3$  and 2.87 %  $\text{NH}_3$ . On further addition of  $\text{NH}_3$  the solution keeps the composition  $b$  as long as the complex remains within the threephasetriangle  $b . D_{2.1.1} . \text{As}_2\text{O}_3$ , and we have the complex:  $\text{As}_2\text{O}_3 + \text{NH}_4\text{AsO}_2 + \text{solution } b$ . The only thing that happens on addition of  $\text{NH}_3$  is the conversion of  $\text{As}_2\text{O}_3$  into  $\text{NH}_4\text{AsO}_2$ . When all the  $\text{As}_2\text{O}_3$  has disappeared and has been converted into  $\text{NH}_4\text{AsO}_2$ , then on further addition of  $\text{NH}_3$  the solution follows curve  $bcd$ , in which case its content of  $\text{As}_2\text{O}_3$  decreases continuously.

*Leiden, Anorg. Chem. Lab.*

**Chemistry.** — “*The allotropy of potassium.*” I. By Prof. ERNST COHEN and Dr. S. WOLFF.

1. We have in view to investigate here whether potassium as it has been known hitherto is a metastable system in consequence of the simultaneous presence of two or more allotropic forms of this metal.

It will become evident from the following lines that the literature already contains very accurate data for solving this problem.

2. As long as thirty years ago ERNST HAGEN<sup>1)</sup> published his very careful experiments on the determination of the coefficient of expansion of potassium, which were carried out with the dilatometer.

Contrarily to many other physicists he bestowed much care on the purity of the material used. The specimen of potassium experimented with contained only a *trace* of sodium (in 6 or 7 grams).

3. For a description of the details of the measurements the reader is referred to the original paper, but it may be pointed out here that the agreement between the determinations made with two different dilatometers (containing  $\pm 40$  grams of potassium each) was exceedingly satisfactory.

The measurements are summarized in the Tables I and II, where  $t$  indicates the temperatures at which the experiments were made, while  $v$  indicates the volume (in ccm.) of 1 gram of the metal.

<sup>1)</sup> Wied. Ann. **19**, 436 (1883).

TABLE I.  
Dilatometer 1.

$t$	$v$	$t$	$v$
0°	1.15665	59.8	1.19170
17.3	1.16148	59.8	1.19457
40.5	1.16823	60	1.19643
			tot
50.1	1.17108	60.1	1.19719
50.2	1.17110	60	1.19734
19.6	1.16238	59.7	1.19593
31.2	1.16542	59.6	1.19353
41.1	1.16829	64.6	1.20480 (liquid)
49.7	1.17097	54.25	1.17452 (solid)
55.1	1.17607		
58.2	1.18611		
19.7	1.16199		
0	1.15650		
52.7	1.17277		
52.8	1.17258		
52.85	1.17259		

TABLE II.  
Dilatometer 2.

$t$	$v$	$t$	$v$
0°	1.15692	59.8	1.19348
17.35	1.16168	59.8	1.19693
40.7	1.16843	60	1.19877
49.9	1.17125	60.1	1.19949
50.2	1.17137	60	1.19976
50.1	1.17134	59.7	1.19918
18.2	1.16211	59.6	1.19575
31.3	1.16587	64.6	1.20495 (liquid)
41.1	1.16863	54.25	1.17611 (solid)
49.7	1.17129		
55.1	1.17712		
58.2	1.18755		
19.7	1.16223		
0	1.15680		
52.7	1.17341		
52.8	1.17312		
52.85	1.17317		

4. In order to calculate the coefficients of expansion, HAGEN only used the observations between 0° and 50° C. He found that the coefficient increases rapidly above 50° C.; there is between this temperature and the melting point an increase of volume of 0.5 per cent which is followed by a sudden increase of 2.5 per cent at the melting point (62°.1).

5. In order to get a clear survey of the phenomena the results of those determinations which were carried out with *both* dilatometers at the *same* temperatures are summarized in Table III. The fourth column contains the differences of volume (in hundredths of a mm<sup>3</sup>) of 1 gram of potassium which is found with the two instruments at the same temperature.

TABLE III.

Temperature	Volume of 1 gr. of potassium in Dilatometer 1	Volume of 1 gr. of potassium in Dilatometer 2	Difference (hundredths of mm. <sup>3</sup> )
0°	1.15665	1.15692	27
50.2	1.17110	1.17137	27
50.1	1.17108	1.17134	26
41.1	1.16829	1.16863	34
49.7	1.17097	1.17129	30
55.1	1.17607	1.17712	105
58.2	1.18611	1.18755	144
19.7	1.16199	1.16223	24
0	1.15650	1.15680	30
52.7	1.17277	1.17341	64
52.8	1.17258	1.17312	54
52.85	1.17259	1.17317	58
59.8	1.19170	1.19348	178
59.8	1.19457	1.19693	236
60	1.19643	1.19877	234
60	1.19734	1.19976	242
59.7	1.19593	1.19918	325
59.6	1.19353	1.19575	322
64.6	1.20480 (liquid)	1.20495 (liquid)	15
54.25	1.17452 (solid)	1.17611 (solid)	159

6. As long as the dilatometers have not been exposed to temperatures higher than 53°, the differences remain small and nearly constant (24—34 units). At higher temperatures they become large (up to 325 units). However, if we go back to 0° C., the difference has become the same (30 units) as it was before at the same temperature. From these data it follows that there has occurred in one dilatometer or in both a *reversible* transformation. That it has taken place in the *solid* metal, is evident from the fact that the difference is again very small (15 units) after the metal has been melted (at 64°.6 C.). If the metal is now cooled to 54°.25 (at which

temperature it is solid), the large differences (159 units) are observed again <sup>1</sup>).

7. If we consider the phenomena with one of the dilatometers (for example with N<sup>o</sup>. 1) it is evident that at the *constant* temperature of 59°.8 C. there occurs an increase of volume (287 units). Some time later the volume at 59°.6 C. is 183 units greater than before at 59°.8 C. although the temperature is lower (0°.2).

8. Considering that in the second dilatometer also the same phenomena occurred at 59°.8 C. [the volume increases at constant temperature (345 units) and is afterwards at 59°.6 C. greater (227 units) than before at a temperature which is 0°.2 lower] we may conclude that the transformation has taken place in *both* dilatometers. (Comp. § 6).

9. These experiments consequently prove that potassium can undergo transformation into a second modification ( $\beta$ -Potassium) and that the metal as it has hitherto been known is at ordinary temperatures a metastable system in consequence of the presence of both forms at the same time.

10. The indications found in the earlier literature that this metal is able to crystallize as well in the regular as in the tetragonal systems <sup>2</sup>), gains more importance in the light of these results.

11. R. W. and R. C. DUNCAN <sup>3</sup>) found that there existed a large difference between the indices of refraction of two mirrors which had been formed from molten potassium. Fresh experiments are wanted in order to decide whether these discrepancies are to be attributed to the presence of different quantities of the two modifications in the mirrors experimented with.

12. As the change of volume which accompanies the transformation mentioned, is considerable, it will be possible to investigate these phenomena by dilatometric measurements more closely than can be done at present from the data given by HAGEN. We hope to report shortly on this point.

*Utrecht, January 1915.*

VAN 'T HOFF-*Laboratory.*

<sup>1</sup>) If the phenomena were to be ascribed to the melting process, the difference at 54°.25 C. at which temperature the metal is solid, would have been small (30 units), which is really not the case.

<sup>2</sup>) ABEGG's Handbuch der anorg. Chemie 2, (1) 338—339 (Leipzig 1908); Long. Journ. Chem. Soc. 13, 122 (1860).

<sup>3</sup>) Phys. Rev. (2) 1, 294 (1913).

**Anatomy.** — “*The vagus area in camelidae*”. By Dr. H. A. VERMEULEN.  
(Communicated by Prof. L. BOLK).

(Communicated in the meeting of December 30, 1914).

In a previous paper<sup>1)</sup> I demonstrated the relation between the development of the dorsal motor vagus nucleus of some domestic animals with the size and structure of the stomach, as well as with the development of the stomach musculature. In that article I pointed out that the shape of its cell-column differs among our ruminating domestic animals; in the ox, for instance, it reaches its full size midway in its length, whereas in the goat not until past the frontal third part, which circumstance I connected with the fact that the omasus, a strongly developed and highly muscular division of the stomach in the ox, is very poorly developed in the goat. Later I examined the dorsal motor vagus-nucleus of the sheep, which animal has also a small omasus, and found similar proportions as in the goat as regards its form and size. In one respect only did the two cell-columns differ, viz. in the goat,  $\frac{3}{5}$  of the nucleus lie spinally and  $\frac{2}{5}$  of it frontally of the calamus; in the sheep the reverse is found; here, as in the horse and ox,  $\frac{2}{5}$  of the nucleus lie in the closed, and  $\frac{3}{5}$  of it in the open portion of the oblongata. (Series of 321 sections, of which 135 spinal and 186 frontal of the calamus, fig. 1).

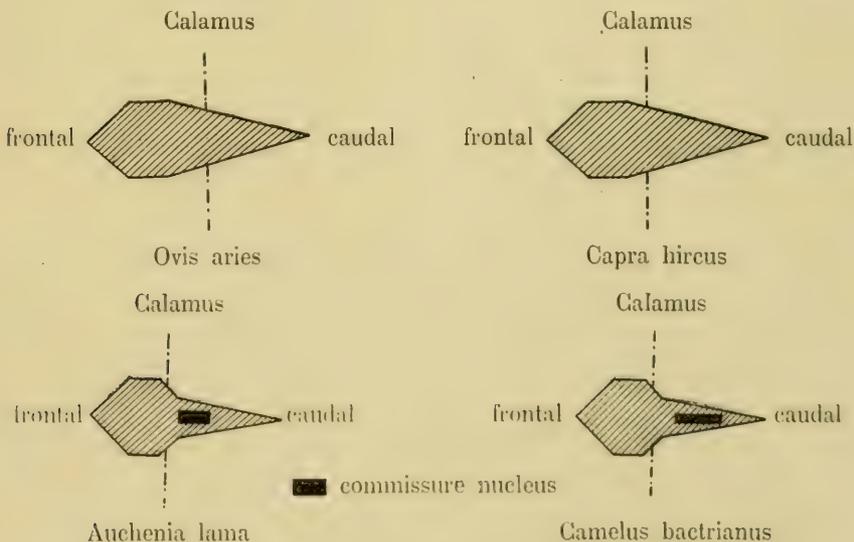


Fig. 1. Dorsal motor vagus nucleus.

<sup>1)</sup> The size of the dorsal motor vagus-nucleus and its relation to the development of the stomach. These Proceedings Vol. XVI p. 305.

I fortunately happened to get hold of the brain-stem of a camel. This ruminating animal is also in the possession of a huge stomach (245 liters capacity) which, however, differs from those of our ruminating domestic animals in many respects. It must be remarked here, however, that the largest of the proventriculi, the rumen, has at both poles a great many (about 50) distinctly separate bulges, each of which can be shut off from the rest of the rumen by a sphincter, and has a capacity of 200 to 300 c.c. These bulges were described by PLINIUS and by many after him as water-reservoirs. Even if this be so, which to an animal of the desert may be considered of great use, it cannot be the only function, for the mucous membrane in these peculiar stomach appendices is richly provided with glands (LESBRE), which points to a digestive function, and at the same time forms a great difference with the inner coating of the rumen in other ruminantia, which have all over a very horny cutaneous mucous membrane. Another remarkable point is that Cameliden have no omasus at all.

The Central Institute for Brain Research at Amsterdam, enabled me to further prosecute my researches. From the above-mentioned Institute I obtained the brainstem of another Camelide, a lama, for which I offer my thanks.

The research was not limited to the dorsal motor vagus-nucleus; other nuclei have also been examined, in particular the nucleus accessorii and the nucleus ambiguus. Special attention was paid to the two last nuclei, in the first place because, according to LESBRE's researches, the nervus accessorius spinalis does not occur in Camelidae, and in the second place because in these animals the nervus laryngeus inferior has no obvious recurrent course.

In his "Recherches anatomiques sur les Camélidés (Archives du Muséum d'Histoire naturelle de Lyon, Vol. VIII 1903) he says on p. 191: "The spinal nerve (the accessory of Willis) is completely wanting; the sterno-mastoideus, mastoido-humeral, omo-trachelian and trapezius muscles receive their double innervation, sensory and motor, from the cervical pair. The absence of the spinal accessory nerve in Camelidae is an anatomical fact of great importance hitherto unknown." A number of root-fibres issuing behind the nervus vagus unite into a declining stem of 3 to 4 cm. in length. This little stem, running to the jugular ganglion, is considered by LESBRE as being the only part present of the nervus accessorius, the nervus accessorius vagi.

From his description of the innervation of the pharynx and the larynx it will be seen that in Camelidae the ramus pharyngeus vagi and the three laryngeal nerves, the nervus laryngeus externus for

pharynx musculature and the musculus cricothyroideus, the nervus laryngeus superior and the nervus laryngeus inferior (recurrens) rise from one stem, in such a way that this stem soon divides into two branches, one of which splits into the two first-named nerves, and a third descending branch, which gives off a ramus oesophagaeus, besides the nervus laryngeus inferior. This last describes a slight curve before reaching the larynx, is thus also recurrent, though not in the ordinary sense of the word.

This unusual course of the nervus recurrens is quite contrary to what has been hitherto assumed in favour of the phylogenetic and ontogenetic development of this portion of the peripheral nervous system. In amphibians, which possess only one cervical vertebra, the heart is situated caudo-ventrally from the larynx. The nervi laryngei inferiores reach the larynx behind the large blood-vessels which come from the heart. With the development of the neck, the heart changes its place in a caudal direction and causes the above-mentioned nerves to descend with it and to reach their territory of innervation by a long recurrent course. LESBRE, who in his detailed treatise, gives a very clear illustration of the devious course of these nerves in Camelidae, is of opinion that the ordinary recurrent course of the nervi laryngei inferiores has been sacrificed to the unusual length of neck in these animals, and expresses the desirability of investigations as to whether similar differences are to be seen in the giraffe.

This fact, meanwhile, implies that the nervus laryngeus inferior in Camelidae has much less to do than in other animals which possess a genuine recurrens in which also more elements are joined.

Of both Camelidae the vagus area was cut serially into sections of 18 microns; that of the camel was coloured with cresyl-violet and that of the lama with toluidineblue.

*Camelus bactrianus.* The region of the *dorsal motor vagus nucleus* is cut into a series of 571 sections, of which 365 are spinal and 206 frontal from the calamus, so that, as in the goat about  $\frac{3}{5}$  of the nucleus lie in the closed portion and  $\frac{2}{5}$  in the open part of the oblongata (fig. 1). The nucleus begins caudally as a narrow horizontal row of cells, dorso-lateral from the canalis centr. in a region where the anterior horns of the cervical cord are still in full development. The nucleus increases slowly, and principally at its lateral side; 70 sections more frontally, before any distinct cells of nucleus XII are present, we see also the medial side becoming slightly thicker, and in the bridge which connects the nuclei right and left, dorsally from the central canal, a few cells occur, of the

same type as those of the vagus nuclei. More frontally the cells in the connecting bridge increase in number and soon both vagus nuclei form with the motor commissural nucleus, dorsally from the central canal, an elongated transverse nucleus column which thickens at both sides. In several sections this transverse cell-column is of uniform thickness, with the exception of the extremities, where the connection with the lateral nuclei occurs. (fig. 2). Ninety sections caudally from the calamus the connecting nucleus ceases, the lateral side of the dorsal motor vagus nucleus is then noticeably thicker and towards the calamus this side dips in a ventro-lateral direction (fig. 3). Here too, as in other animals, it may be noted that in the ventro-lateral portion of the nucleus, numerous cells occur of a larger type than in the rest of it.



Fig. 2.

X Dorsal motor vagus nuclei and commissural motor X nucleus in the camel; *b* = bloodvessels, *c* = canalis centralis.



Fig. 3. *a* = aberrant bundles, *b* = bloodvessels.

A *nucleus motorius commissuralis vagi* has never yet been met with in any other animal: as we shall presently see it also occurs in the lama. The connecting nucleus lies principally in the region of the commissura infima, the decussation of the tractus solitarii, the sensory glossopharyngeo-vagus tracts.

In the calamus the dorsal motor vagus nucleus has grown thicker; it then contains about 70 cells of the mixed type, the larger of which lie for the most part ventro-laterally. Frontally from the calamus the dorso-medial portion broadens out so that the nucleus becomes triangular in form with the base of the triangle turned towards the ependyma (fig. 4). In the frontal third part of the nucleus 170 cells can be counted in many of the sections, frequently we see the large-celled type in groups together in the ventro-lateral



(the figure is reversed ; it represents the left side)

Fig. 4. *a* = aberrant bundles, *b* = bloodvessels.

Fig. 5. *b* = bloodvessels.

portion. As usually the nucleus decreases here first in its dorso-medial portion, a thin column, which creeps up the ependyma, is preserved longest and, as the ventral portion is well developed there, the nucleus in this region shows the form of a pyramid, with the apex pointing upwards. (fig. 5).

The dorsal motor vagus nucleus of the camel does not reach to the level of the facialis nucleus, as is the case in several other mammals.

At the spinal extremity of the dorsal motor vagus nucleus in the camel, the *nucleus accessorius* is still clearly visible rather more ventral and decidedly lateral, in the substantia reticularis. It can even be seen on a level near the caudal extremity of the nucleus XII. (fig. 6).

Here the accessorius nucleus is very unequally developed, frequently but few cells are found; but we may see a more or less round group of the familiar large cells, at the most 20—24, very

strongly developed. In several preparations intermediate cells are to be seen between the nucleus accessorius and the dorsal motor vagus

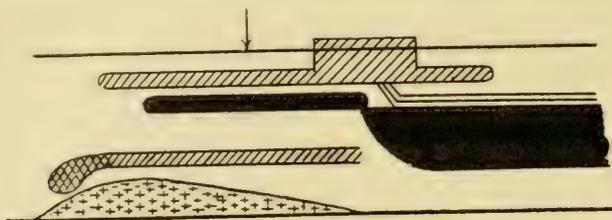


Fig. 6. *Camelus bactrianus*.<sup>1)</sup>

EXPLANATION:

↓ = Calamus       = *Oliv. inf.*       = nucl. IX

 = nucl. X       = nucl. XI       = nucl. XII + Cernic I

nucleus (fig. 7). Here, too, in several sections ventro-lateral outgrowths of the accessorius nucleus are present, which might give the impression



Fig. 7.

as if this nucleus in the camel continues directly into the nucleus ambiguus. This, however, can be proved not to be the case, since the ambiguus shows itself much more ventro-laterally. In a few sections both the accessorius nucleus and ambiguus are present<sup>1)</sup> (fig. 8) and their separate character is then easily seen. As the remainder of nucleus XI we frontally see a small cluster of cells medial from the ventral border of the radix descendens nervi V. The fact that the ambiguus in a more frontal plain is also found near this border, explains the old theory that the ambiguus is a continua-

<sup>1)</sup> In this diagram (Fig. 6) the caudal extremity of the nucl. ambiguus is a little shortened for clearness sake.

tion of the accessorius nucleus. The rad. descend. V is, however, more developed in the oblongata, and its ventral border comes to lie in a much lower region. Ambiguus and accessorius nucleus are both derivatives of the dorsal motory vagus nucleus. This has been proved phylogenetically and ontogenetically by KAPPERS, and is again confirmed in the camel by the intermediate cells between the dorsal motor X nucleus and the nucleus XI and the simultaneous but distinctly separate presence of the latter and the nucleus ambiguus on the same transverse level.

The *nucleus ambiguus* of the camel is, with the exception of its frontal pole, but slightly developed. In the closed part of the oblongata it shows no more than 10 to 12 cells in one section and very frequently none at all are to be found. This holds good also for the rest, with the exception, as said above, of the frontal pole. On a transverse level corresponding with the frontal end of nucleus XII, we still find clusters of 4—6 large ambiguous cells, while on the other hand, on the level corresponding with the frontal pole of the dorsal motor vagus nucleus, the nucleus ambiguus enlarges very rapidly to an immense complex of cells in which a maximum of 80—85 cells



Fig. 8.

Showing the separate character of the nucleus accessorius and nucleus ambiguus:



Fig. 9.

Frontal enlargement of the nucleus ambiguus in the camel.

may be counted. Frontally the enlarged nucleus ambiguus can be divided into a medial portion with smaller and a lateral portion with larger cells. While the frontal enlargement of the ambiguus (where it occurs) is generally described as a mass of closely crowded cells of smaller type than the ordinary ambiguous cells, it is here remarkable that the cell group is not so crowded together and contains, especially in the lateral portion, typically large ambiguous cells (fig. 9).

Its frontal extremity has clearly shifted ventrally. It is 54 sections long and extends 30 sections frontally from the dorsal motor vagus nucleus (fig. 6). Twelve sections further the nucleus VII begins.

Concerning the *hypoglossus nucleus* it may be mentioned that its

caudal extremity is not easily determined, efferent hypoglossus roots can be observed very far caudad and it is frequently seen that, frontally from sections in which XII cells are present, ventral horn cells again appear; a sharp boundary between ventral horn and hypoglossus nucleus is not present (fig. 6). Also, it can be seen in several of the sections that cells have shifted from the vagus column ventrally to near the hypoglossus region (fig. 7), a position which strongly resembles that in birds. The first constant XII cells appear dorsally, close to the dorsal motor vagus nucleus, then the medial group of XII cells appears and finally its ventro-lateral group. Spinally from the calamus, the three groups of XII cells are not clearly defined and one or two groups of it are rather poorly developed. Frontally from the calamus the grouping is clearer and also central cells occur. The dorso-lateral group is most strongly represented and is the most constant, the other groups are in several sections less strongly developed. Frontally the dorso-lateral group disappears first, and the ventral remains longest.

The hypoglossus column extends 134 sections frontal from the calamus.

The *oliva inferior* of the camel is poorly developed. It appears with a ventral lamella, rather ventro-lateral, on the transverse level of the spinal pole of the nucleus XII. This ventral lamella spreads medially and then creeps up the raphe. The second lamella lying dorsally and representing the olivary nucleus *sense strictiori* does not appear before in the neighbourhood of the calamus. At the frontal pole of nucleus XII, it becomes thicker; it ends rather frontally from the ambiguous swelling (fig. 6). Its cell type is small, the cells being thinly sown in some places.

The exceedingly poor development of the *nucleus reticularis inferior* is striking. Very few cells occur in the raphe, most of them frontally in the ventral portion.

In the series of this camel, through the whole vagus region, at the left side, an *aberrating descending bundle* is seen. In the acoustic region we see cross-sections of a few small sharply outlined bundles, under the lateral ependyma, of the IV ventricle. At the right side we find at that place one little bundle. Caudally the bundles on the left side increase greatly in number and their diameter varies greatly. At the frontal pole of nucleus X dorsalis the bundles are crowded into a wedgeshape between the cells of this nucleus: fig. 4 (This figure is reversed, it represents the left side). An ascending bundle of fibres, beneath the ependyma runs in a dorsal direction along the top of the vagus nucleus; more caudally a ventral branch also appears, which runs medially from

the XII nucleus in the direction of the raphe. Near the calamus 40 bundles can be counted on the left side; at the right, where a few more are added, only 3 or 4 are to be found. The dorsal branch of the bundles has disappeared; caudally from the calamus the complex runs ventrally from the dorsal motor vagus nucleus and medially from the central canal (fig. 3). The complex gradually decreases, its outline finally fades away and 170 sections spinally from the calamus the last bundle disappears in the raphe. Regarding the exact connections of the latter I do not venture to make any statement.

*Auchenia lama*. Series of 365 sections; the calamus falls in section 219, so that here too, as in the goat and the camel,  $\frac{2}{3}$  of the *dorsal motor vagus nucleus* lie in the closed part of the oblongata (fig. 1). The nucleus begins caudally as a small, round group of cells, dorso-lateral from the canalis centralis; it increases slowly in size chiefly at its lateral side, so that it becomes egg-shaped, not before the middle of the spinal portion does it become more oblong in shape and the first commissure cells appear, frequently lying more dorsally than in the camel, so that the whole cell-column, dorsally from the central canal takes a more or less curved course. (fig. 10).

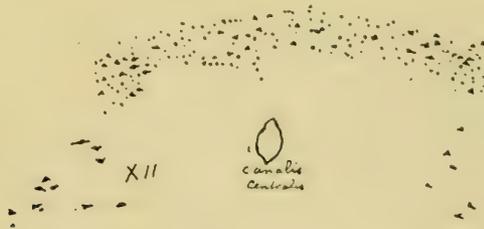


Fig. 10. Dorsal motor vagus nuclei and motor commissural X nucleus in the lama.

The *motor commissural vagus nucleus* of the lama (Fig. 10) is in general not so well developed as that of the camel. Although it stretches further frontally than in the camel (ending 20 sections spinally from the calamus) it is smaller in comparison (fig. 1). Its size is not constant, in some places it is more or less poorly developed.

In the lama too, the dorsal motor vagus nucleus lies obliquely near the calamus, and it has a much thicker ventro-lateral pole, containing many cells of the large type; in front of the calamus the dorsomedial part also bulges distinctly, and the nucleus thereby becomes triangular in shape, with the base directed towards the

bottom of the ventricle; more frontally it loses this form because the ventro-lateral pole also enlarges, after which the structure of the nucleus becomes looser and the number of cells grows less. Here too, the ventro-lateral portion remains longest, and the dorsal motor vagus nucleus does not reach into the region of the nucleus facialis.

The *nucleus accessorii* lies more medially into the lamat han in the camel, just on the border of the anterior and posterior horns. Near the spinal pole of the dorsal motor vagus nucleus it is well developed; in some sections  $\pm 90$  large XI cells, and medially from this, in the same level, 5—8 dorsal vagus cells can be counted (fig. 11). Very soon a tendency can be observed in the XI nucleus to extend medially; in one section it contains as many as 35 large cells and it is clearly prolonged in the direction of the dorsal motor vagus-nucleus;



Fig. 11. *A* posterior horn, *B* anterior horn.



Fig. 12. *A* posterior horn, *B* anterior horn, *C* canalis centralis.

immediately after the two nuclei join to one large group containing 55 cells, of which the most medial ones have kept the smaller type of the dorsal vagus cells, whereas the lateral cells exhibit the large accessorius-nucleus type (fig. 12 and 14). This constellation soon decreases in size and is only to be seen in 4 consecutive sections after which the vagus nucleus remains in its usual extent at that place; it contains then about 30 cells of mixed type; the large cell-type remains principally lateral. After this on more frontal levels with a very few exceptions nothing more of the nucleus accessorii is to be seen. Near the spinal extremity of nucleus XII, however, the process repeats itself to a slight extent, and we see a few XI cells rise and shift in a medial direction<sup>1)</sup>. As far as the material at our disposal extended, i.e. 165 sections spinally from the beginning of the dorsal

<sup>1)</sup> Not indicated in the diagram of fig. 14.

motor vagus nucleus, the XI nucleus did seem to be constantly present and was very unequally developed. In the very first sections, however, it could be seen; on an average it contains here 8—20 cells.

Concerning the *nucleus ambiguus* it may be said that in general this is better developed in the lama than in the camel. It begins caudally from the place where the nucleus XII is clearly present and where the anterior horns of the cervical cord are still visible. More frontally it soon enlarges, but soon decreases again, and occurs but very slightly in the calamus region. In the open part of the oblongata its appearance is very different; as far as the frontal pole of nucleus XII its ventro-lateral part is generally the most strongly developed; occasionally the nucleus then contains 20—25 cells. As far as the frontal pole of the dorsal motor vagus nucleus, the development is again very poor, after which we see a round group of 8—10 cells arise that enlarges greatly on a level frontal from the dorsal vagus nucleus. Originally two cell groups can be distinguished in the frontal enlargement, but very soon these join to form one large complex, containing at the most 75 cells, mostly of the large type; the majority of the large cells are here also found in the lateral part (fig. 13). Also this enlargement of the nucleus ambiguus distinctly lies in a more ventral plane than the rest of the nucleus;



Fig. 13.

Frontal enlargement of the nucleus ambiguus in the lama.

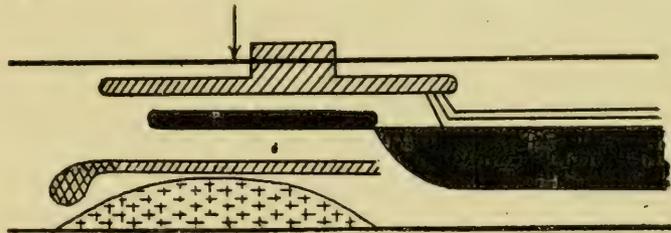


Fig. 14. Auchenia lama<sup>1)</sup>.

(Explanation as in figure 6.)

as is usually the case in lower mammals. It projects 56 sections in front of the frontal extremity of the dorsal motor vagus nucleus (fig. 14) and it is in this region that the first cells of the nucleus facialis appear.

Also in the lama the connection of the *nucleus hypoglossi* with the anterior horn of the cervical cord be observed (fig. 14). Behind the calamus, the XII nucleus is poorly developed in this animal, and a division into groups can hardly be observed here. Frontally from the calamus the medial group appears, and soon after also the

<sup>1)</sup> In this diagram (Fig. 14) the caudal extremity of the nucl. ambiguus is a little shortened for clearness' sake.

ventro-lateral group. The nucleus is now well developed; the dorso-lateral part lies more ventrally than in the camel, so that we better speak of a dorsal group and a ventro-lateral group in this animal. More frontally the medial group becomes thicker and then contains cells of a larger type than those behind. The dorso-lateral group first disappears, and then the medial, so that the large cells of the ventro-lateral group remain longest visible.

The nucleus extends 116 sections in front of the calamus.

The *oliva inferior* is much better developed in the lama than in the camel. Also here it occurs latero-ventrally in the region of the spinal part of nucleus XII. It contains more cells than that of the camel, and the cell type in general is larger. On the level of the frontal pole of nucleus X dorsalis it is still clearly present; it decreases rapidly and ceases at the frontal extremity of the nucleus ambiguus (fig. 14).

The *nucleus reticularis inferior* is extremely well developed in the lama. It grows dorsally over the olive and spreads medially from the raphe into the substantia reticularis. A clearly defined cell group lies under the efferent vagus root. This disappears first, and the rest near the region of the nuc. facialis.

The dorsal motor vagus nucleus of Camelides lies, as in all other animals, in a region, that is rich in blood-vessels. All the illustrations of it, which occur in this article and which have been made after microphotographs, show cross-sections of large blood-vessels.

The form of the nucleus differs in Camelidae as well as in the sheep and goat, from that in the cow in so far as in the last-named animal it attains its greatest extent on the half of its extent, while in the first-named animals it does so not before the frontal third part. Since in the cow  $\frac{2}{5}$  of the nucleus lies spinally from the calamus, the most developed part of the nucleus, which at this place is clearly less in size in other ruminantia, begins just frontally from the calamus and we must therefore look for the centre of the innervation of the omasus in the most caudal portion of the fossa rhomboidea, at least in the ox and sheep. In the goat and in Camelidae, where a larger part of the nucleus stretches into the closed portion of the oblongata than in the first-named animals, that centrum may stretch, or at least partially, somewhat spinally from the calamus.

LESBRE has shown that a *nervus accessorius spinalis*, such as we know in all other mammals hitherto examined, as a nerve which arises from a nucleus of its own in the cervical cord and runs

upwards united between the roots of cervical nerves, does not occur in Camelidae, and says of this that it is "un fait anatomique de haute importance". I have, however, proved that a spinal *nucleus accessorius* does really occur in these animals. It must a priori be considered as extremely doubtful that an anatomical centre which occurs so constantly in mammals should be absent in these animals. Undoubtedly it is highly remarkable *that the spinal accessorius fibres are not united in these animals to one stem but physiologically this cannot be regarded as a fact of "haute importance"*, since also in these animals spinal accessorius fibres reach their destination, though more directly with cervical nerves, and not by a detour.

In all anatomical text-books the *nervus accessorii Willisii* will be found described as consisting of two parts, a *spinal* and a *bulbar part*, the latter (because it unites wholly or partly with the *nervus vagus*) being called also the *nervus accessorius vagi*. The distinction is based on the fact that in man the *accessorius spinalis* and *accessorius vagi* unite into one stem, viz. the *nervus accessorius communis*, after which the bulbar part separates again to join the *vagus* after this nerve has passed the jugular ganglion. RAMON Y CAJAL says meanwhile in his "Histologie du système nerveux de l'homme et des vertébrés" (Vol. I, p. 719) that he shares the opinion of KOSAKA that this division into an *accessorius spinalis* and *bulbaris* has no significance, since they are convinced that a bulbar *accessorius* does not exist, but that the latter originates in the dorsal motory *vagus nucleus* and thus contains ordinary *vagus fibres*.

I do not agree with CAJAL and KOSAKA, though their view seems to be proved by the fact that in domestic animals the two parts of the *nervus accessorius* do not unite into *one stem*, e.g. in the horse the front part of the *pars bulbaris* enters the *ganglion jugulare*, while only the hindmost part joins the *accessorius spinalis*; in ruminants and carnivora, on the other hand, the entire *accessorius bulbaris* enters the *ganglion jugulare*, while in the pig this part reaches the *nervus vagus* late, viz. at the place where the *ramus pharyngeus* is given off. On account of my observations, however, in the camel and in the lama, I have come to the conclusion that *accessorius cells* really do occur in the *oblongata*. In these animals the *accessorius nucleus* is very distinct in the region of the dorsal motor *vagus nucleus*; in the lama it immediately joins the aforesaid *vagus nucleus*, in the camel there are only traces of such a connection. In any case, in both animals the *accessorius nucleus* extends into the *oblongata*. I am willing to assume that in the so called *ramus internus n. accessorii*, i.e. in such part of it as joins the *nervus*

vagus, genuine vagus fibres run, but there is no doubt whatever that a part of the nervus accessorius originates in the oblongata. Even the fact that fibres originate in the dorsal motor vagus nucl. does not in my opinion prove that they are necessarily vagus fibres. I consider it remarkable that in all the animals I have examined as yet the dorsal motor vagus nucleus shortly after its caudal appearance exhibits in the lateral part a type of cell which is larger than its original cell-type, a type which is maintained over a part of the nucleus, chiefly at its ventro-lateral and ventral sides.<sup>1)</sup> I venture to express the supposition that these large cells, although they pass over into the dorsal motor vagus nucleus, are accessorius elements. The accessorius nucleus, which has originated ontogenetically and phylogenetically from the caudal part of the dorsal motor X nucleus (KAPPERS<sup>2)</sup>), thus exhibits this relationship in *Camelus* and *Lama* still in the full-grown animal.

The enlargement of the dorsal motor vagus nucleus in Camelide with the motor commissural nucleus may be explained by the striking differences which the oesophagus and stomach of these animals exhibit from other ruminants. Not only is the oesophagus in these animals remarkably long in proportion (in *Camelus*  $\pm$  2 meters!) but this organ is likewise in every respect particularly rich in glands (LESBRE), and, as has already been stated, the rumen contains many glands in some of its divisions. In this connection I may mention that, after I had shown the motor commissural vagus nucleus in *Camelus* and *Lama*, I carefully examined my series of the sheep and the goat in respect to this, and only found in some sections indications of this connecting nucleus, a remarkable symptom, since in these animals glands are but rarely met with in the oesophagus and in a part of the omasus. The position of the nucleus motorius commissuralis vagi in the commissura inferior visceralis which contains descending sensory fibres of oesophagus and stomach must be ascribed to neuro-biotactic influences.

The short course of the nervus laryngeus inferior seems to be correlated with a smaller development of the caudal third part of the nucleus ambiguus. The pronounced development of the frontal enlargement of the nucleus ambiguus, the centre of the motor glossopharyngeus, may be explained by the exceptional

<sup>1)</sup> STUURMAN has also pointed out the occurrence of two celltypes in the dorsal motor vagus nucleus. F. J. STUURMAN, "Over den oorsprong van den nervus vagus bij het konijn." Acad. Proefschrift, Amsterdam. 1913

<sup>2)</sup> Weitere Mitteilungen über Neurobiotaxis, VII. Folia Neurobiologica. Bnd. VI. Sommerergänzungs Heft, p. 94.

length of the pharynx in Camelides (LESBRE). The unusual wealth of glands in the digestive tract of these animals is a result of their mode of living. Numerous plants on which they feed in a wild state are abundantly covered with large strong thorns, so that an extra development of glands in the mucous membranes is really not superfluous for them.

### CONCLUSIONS.

The centre of the innervation of the omasus of the Ruminantia must be looked for in the most caudal part of the fossa rhomboidea or, for a part directly caudally from the Calamus.

In Camelidae an extension of the dorsal motor vagus nucleus occurs in the region of the sensory commissura infima visceralis, so that the motor dorsal X nuclei from the two sides are united (nucleus motorius commissuralis vagi). In the sheep and the goat only slight indications of this connecting nucleus are present.

The nervus recurrens is given off in Camelidae in conjunction with the ramus pharyngeus n. vagi and the nervus laryngeus superior (LESBRE); in accordance with this unusually short course the nucleus ambiguus, especially in the spinal third part, seems to be less developed than in other animals.

The frontal enlargement of the nucleus ambiguus in these animals is particularly strong, and possesses numerous cells of a larger type than are usually met with at that place.

A *nervus accessorius spinalis* is not present in Camelidae (LESBRE); since a *nucleus accessorii* is present in the cervical cord, however, the accessorius fibres must run with the cervical nerves.

An accessorius nucleus is also very clearly seen in the region of the dorsal motor vagus nucleus; since the region of this vagus nucleus is considered to belong to the bulbus, a really bulbar part of the nucleus accessorii has to be accepted, the presence of which has been denied by CAJAL and KOSAKA.

In those sections where in Lama and Camel the nucl. ambiguus and the nucleus accessorius are both present, they remain clearly separated. The nucleus accessorius is not continuous in these animals with the nucl. ambiguus.

In the lama a direct connection of the nucleus XI with the nucleus motorius dorsalis X, as has been observed embryologically (KAPPERS), can be distinctly demonstrated. The accessorius nucleus thus enlarges the vagus nucleus in question at its lateral side with cells of a larger type.

The nucleus XII in Camelidae exhibits very primitive features and has preserved its connection with grey matter of the anterior horn as in lower vertebrates.

In the camel the oliva inferior and the nucleus reticularis inferior are only slightly, in the lama on the contrary rather strongly, developed.

*Utrecht, December 1914.*



**March 26, 1915.**

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING  
of Saturday March 27, 1915.

VOL. XVII.

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

*Secretary:* Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
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CONTENTS.

- S. DE BOER: "On the heart-rhythm". II. (Communicated by Prof. J. K. A. WERTHEIM SALOMONSON), p. 1135.
- P. H. GALLÉ: "On the relation between departures from the normal in the strength of the trade-winds of the Atlantic Ocean and those in the waterlevel and temperature in the northern European seas", (Communicated by Dr. J. P. VAN DER STOK), p. 1447.
- II. R. KRUYT and JAC. VAN DER SPEK: "The connexion between the limit value and the concentration of Arsenic Trisulphide sols". (Communicated by Prof. E. COHEN), p. 1158.
- R. A. WEERMAN: "Action of sodium hypochlorite on amides of  $\alpha$ -oxyacids. A new method for the degradation of sugars." (Communicated by Prof. A. P. N. FRANCHIMONT), p. 1163.
- II. TETRODE: "Theoretical determination of the entropy constant of gases and liquids". (Communicated by Prof. H. A. LORENTZ), p. 1167.
- P. EHRENFEST: "On interference phenomena to be expected when Röntgen rays pass through a di-atomic gas". (Communicated by Prof. H. A. LORENTZ), p. 1184.
- II. A. BROUWER: "On the granitic area of Rokan (Middle Sumatra) and on contact-phenomena in the surrounding schists." (Communicated by Prof. G. A. F. MOLENGRAEFF), p. 1190.
- Errata, p. 1202.

**Physiology.** — "On the heart-rhythm." <sup>1)</sup> II. By Dr. S. DE BOER.  
(Communicated by Prof. J. K. A. WERTHEIM SALOMONSON).

(Communicated in the meeting of February 27, 1915).

*Pulsus bi-, tri- and polygeminus.*

In my former communication I incidentally called the attention to the fact that pulsus bigeminus occurs as a transition-period from the normal heart-rhythm to the halved one. In the following pages I intend to communicate, in what way the normal heart-rhythm can through different intermediate periods pass into the halved one. As an example of this manner of halving the following experiment may serve:

<sup>1)</sup> According to investigations made in the physiological laboratory of the University of Amsterdam.

After about one hundred systoles of a frog's heart had been transferred to the smoked paper, according to the suspension-method, 10 drops of a 1% solution of acetabatrini are injected into the abdominal cavity. The rhythm slackens, the *a-v* interval increases, till half an hour after the injection one auricle- and one ventricle-systole fall out (Vide Fig. I upper-row). Afterwards the 10<sup>th</sup>

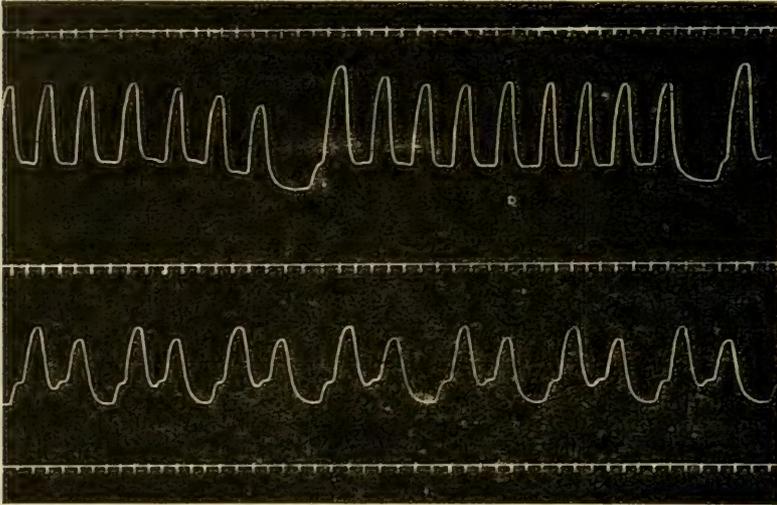


Fig. 1.

Suspensioncurves of a frog's heart poisoned with veratrine; in the upper-row of curves twice one systole of ventricle and auricle fall out.

The lower row of curves shows bigeminus-groups and is reproduced 20 minutes later. Time 1 sec. (just as in all further figures).

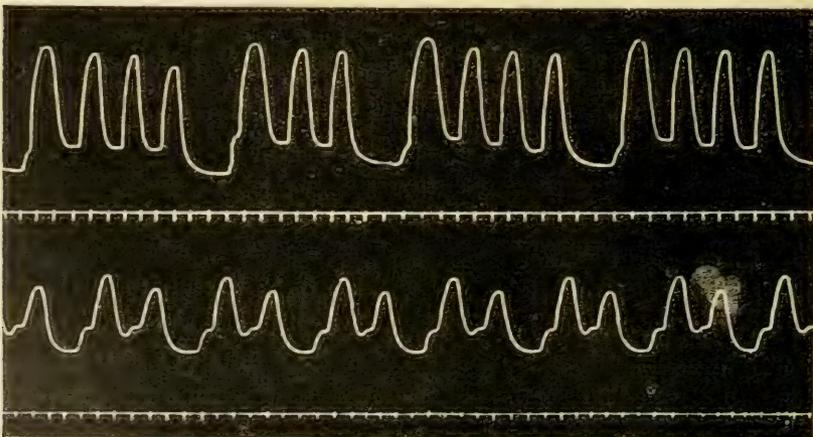


Fig. 2.

Both rows of curves are continuations of those of Fig. 1, but 27 systoles afterwards.

auricle- and ventricle-systoles fall out again (still to be seen in the figure). Thereupon again and again but a little earlier one auricle- and one ventricle-systole fall out. Fig. 2 is reproduced 27 systoles after the former. In the upper row we see here  $\gamma$  quadri- and trigeminus. Then for a short time larger groups occur again. So Fig. 3 is represented twenty systoles after the former. In this figure (upper row

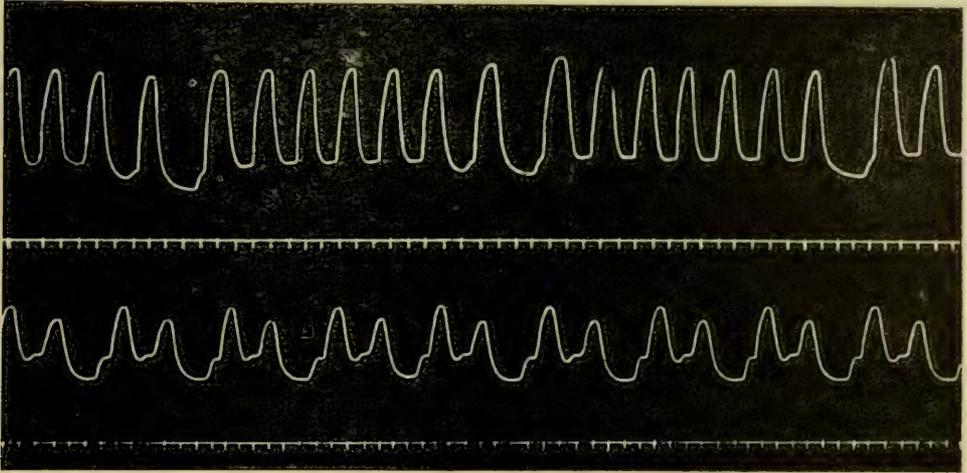


Fig. 3.

Continuation of Fig. 2 but 20 systoles afterwards.

of curves) a special peculiarity can be seen, which I observed on this curve-page only there, and then twice. After the first and also the second falling out of an auricle- and a ventricle-systole (fig. 3) there comes a little later a new auricle- and ventricle-systole. The latter falls entirely beyond the normal heart-period, it is perhaps an extra-systole, originating in the auricle, which has then not caused an irritation of the sinus venosus by retrograde conduction (for the normal heartperiod is not disturbed, whilst the process continues). Another possibility is, that for this curve the conduction in the *si-a*-systems of connection is very slow, and consequently the following auricle is so much retarded.

In this figure again one systole falls out, but now such an abnormally retarded systole does not occur. (3<sup>rd</sup> hiatus in the upper row). If now we measure here the duration from the beginning of the ventricle-systole before the pause to the beginning of the ventricle-systole after it, we find a duration that is much shorter than that of 2 heart-periods.

This difference is caused by the abbreviation of the *si-a*-interval and the *a-v*-interval after the longer pause. Moreover the last ventricle-systole before the pause begins very late, because the con-

duction along these two systems of connection is much retarded. The widening and enlargement of the systoles after the longer pauses is here, as likewise in the other figures, very conspicuous. Fig. 4 is reproduced 150 systoles after the former.

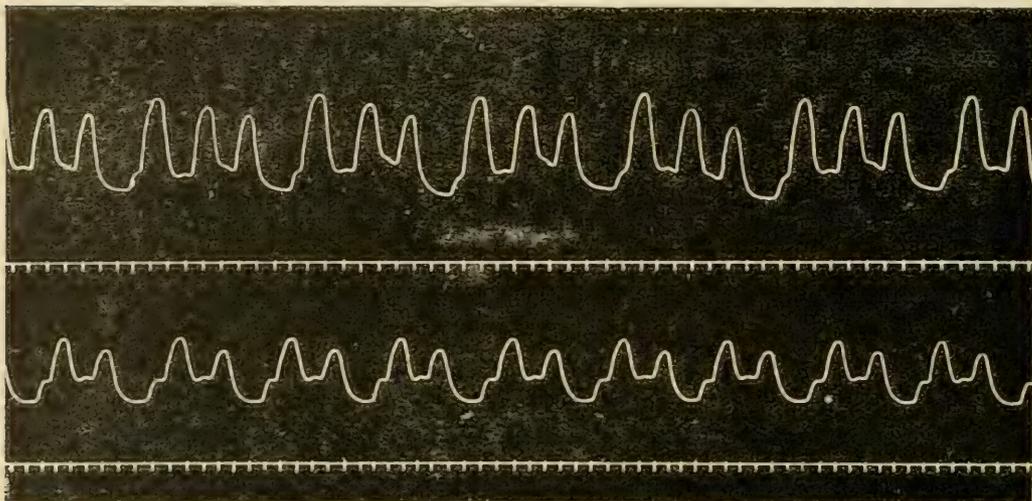


Fig. 4.

Continuation of Fig. 3, 150 systoles afterwards.

In the mean time the groups have become smaller and they now form here trigeminus-groups. In all 4 figures the bigeminus-groups have been reproduced 20 minutes later than the first row.

The second systole of each bigeminus- and the third of each trigeminus-group is always least high and wide. In each group there is consequently a diminution of the dimension of the systoles. From my former communication it is known, that in bigeminus-groups the point and the basis can pulsate alternately. In this case every systole was not a systole of the whole ventricle musculature, but for each of the two systoles every time another part of the ventricle-muscle was in contraction. Consequently there can be no doubt but partial asystole is possible. And so I saw here with every bigeminus-group during the first systole the whole ventricle contract, and during the second the point of the ventricle continued inactive. We must explain this by the fact, that the irritability of the heart-point diminishes here during the groups, so that after every first systole the conducted irritation cannot make it contract. This is likewise true for the trigeminus-groups.

In order to make a more accurate investigation into the cause of the falling out of the first systole (vide Fig. 1) I have measured

the  $a-v$ -interval of the last 6 systoles before the hiatus, and of 8 after it. The numbers

before the hiatus are:	after the hiatus are:
0,9 sec.	0,7 sec.
1,0 „	0,9 „
1,1 „	0,95 „
1,1 „	0,95 „
1,1 „	0,95 „
	1,0 „
	0,95 „
	0,95 „

Consequently we see that the  $a-v$ -interval increases in duration, whenever a ventricle- and an auricle-systole fall out. After the hiatus the  $a-v$ -interval is smaller, and afterwards increases again in duration.

Further I fixed the duration of the beginning of each ventricle-systole to the beginning of the next following auricle-systole. As variable quantities in these measurements must be taken into consideration in the first place the retardation or anticipation (by increase or decrease of the intervals  $si-a$  and  $a-v$ ) of the ventricle systole with which I began the measurement, and then the retardation or anticipation of the beginning of the following auricle-systole (through modification caused in the velocity of conduct between  $si$  and  $a$ )<sup>1)</sup>. Beginning with the 6<sup>th</sup> systole before the first hiatus this duration for this systole and the following one amounted to:

1,8  
 1,8  
 1,8  
 1,8  
 1,8  
 3,4 (at the first hiatus)  
 2,1  
 1,9  
 1,8  
 1,8  
 1,9  
 3,7 (at the second hiatus)  
 2,1

<sup>1)</sup> Where I speak of the time of conduction between  $si$  and  $a$  and between  $a$  and  $v$ , I understand by it the time required for the stimulation to transmit itself along the systems of conduct + the time, that the stimulation requires to influence the atrium resp. the ventricle.

If now we examine more closely the number 3,4 i.e. the distance from the beginning of the last ventricle-systole before the hiatus to the beginning of the first auricle-systole after this, we must take into consideration that this includes the duration of one entire ventricle-period + the duration of the beginning of one ventricle-systole to the beginning of the following auricle-systole. The duration of a heart-period is 2,75 sec. This subtracted from the duration of 3,4 sec. which we found, gives 0.65 sec. If now we compare this number with the others of the above list we see that it is about  $\frac{1}{3}$  part of it. The cause of this short duration is in the first place the retardation in the conduct systems (*si-a* and *a-v*) which made the last ventricle-systole before the hiatus begin very late; after the hiatus the conduct *si-a* has much improved, by which the beginning of the first auricle-systole after the hiatus is anticipated. The co-operation of these two factors has consequently reduced the number we found to one third.

The following number of the list, on the contrary, is again much greater; the anticipation of the first ventricle-systole after the hiatus is the cause of it. The number we found for the second hiatus is 0.3 second greater than the equivalent number for the first hiatus. This means that now less repair of conduct takes place in the connection-systems *s-a* than at the first falling out of a heart-period. After this the next following number is also again greater than usually. At first it seems astonishing, that this number is again as great (2,1 sec.) as after the first falling out. If the increase of this number is caused by the anticipation of the preceding systole, this number ought to be inferior here; for the preceding systole is here less anticipated than after the first hiatus. We must however not forget that, on account of the better conduct in the connection-systems the second ventricle-systole has also been a little anticipated, and that this anticipation is now less important than after the first hiatus.

It appears with certainty from the measurements I made also for the following hiatuses, that the repair of conduct in the connection-systems becomes constantly worse. This is the cause that a heart-period must constantly sooner fall out. The fact that the repair of the irritability of the heart-muscle constantly diminishes, and consequently the duration of the refractory period, directly after an hiatus, decreases less, will certainly have its influence in this respect. In the further progress of the curves we see indeed that the heart-periods fall out sooner. In this respect I made still a great number of measurements, for the sake of brevity I do not mention these here. From all these measurements the repair of conduct after the

falling out of a heart-period appeared distinctly. I will just fix the attention to one deviation that I detected. When I fixed in the bigeminusgroups the  $a-v$ -interval, calculated from the beginning of the auricle-systole to the beginning of the ventricle-systole, I constantly obtained for the large ventricle-systole, occurring after the hiatus, a greater value than for the next little second systole.

This would consequently be entirely in contradiction with the irrefutable fact, that after longer pauses this interval decreases. I think, I am able to indicate the cause of this phenomenon, it is of a pure technical nature, and depends upon the manner of registering. The first ventricle-systole of each bigeminus-group begins in the beginning of the diastole of the preceding auricle-systole. Consequently the entire heart is lengthened at the beginning of this ventricle-systole by the then allongating auricle, and shortened by the ventricle which at the same time passes into systole. The beginning of the systole is consequently only expressed in the curve, as soon as the shortening of the ventricle prevails; this causes the retardation. This is not the case with the second ventricle-systole of every bigeminus-group, because the ventricle-systole begins later, and moreover the preceding auricle-systole during this process is very little. I did not

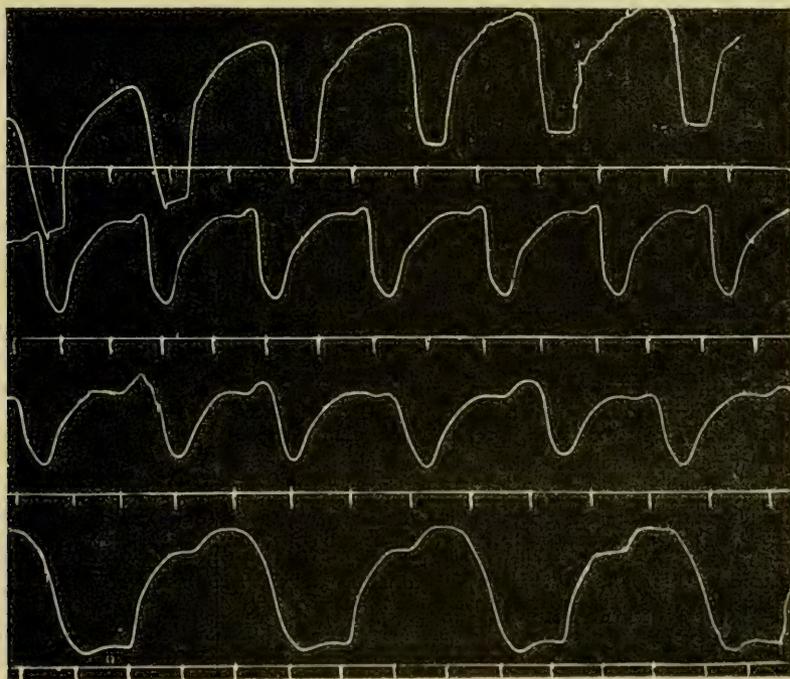


Fig. 5.

In the curve-row 3 the reproduction of the curves of the auricle-systoles changes, as soon as these occur in the beginning of the ventricle-systole.

discover this deviation of the  $a-v$ -interval directly after the larger pauses for the poly- and trigeminusgroups. The reason of this phenomenon is, that here the ventricle-systole begins during the systole of the preceding auricle (vide Figs. 1, 2, 3, and 4). Consequently these two shortenings sum up and the systole of the ventricle is not retarded in the curves. From this it appears again, that the repair of conduct in the connection-systems becomes constantly worse after the falling out of one systole. Till the trigeminus-groups (these included) the first ventricle-curve after a hiatus begins during the systole of the preceding auricle; with the bigeminus-groups the first ventricle-systole begins during the diastole of the preceding auricle-curve. (I can explain with another example the fact, that the curve of the systole of one partition of the heart changes entirely, when at the same time another partition of the heart is in diastole (vide Fig. 5).

The third row of curves is here represented 45 min. after the injection of 5 drops of 1% acetabatrini. Here the auricle-systole begins at the 3<sup>rd</sup> and 5<sup>th</sup> curves in the beginning of the diastole of the ventricle, and then, as it were, it sinks entirely away; if, on the contrary, the auricle-systole begins at the top, then it is much larger. This piece has been photographed from a row of 2½ m. in length, in which, whenever the auricle occurs in the beginning of the ventricle-diastole, the latter decreases. In the following row of curves the rhythm is halved, and an everywhere equal auricle-systole is represented on the ventricle-curve.)

I have thus noted for 1½ hour bigeminus-groups of this heart;

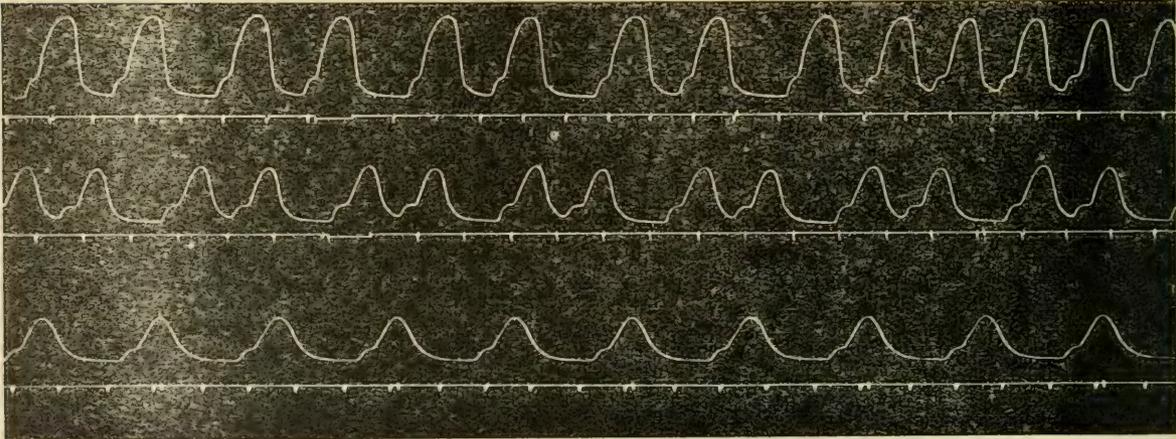


Fig. 6.

Transition from *p* bigeminus into the normal rhythm, then again *p*. bigeminus and afterwards halving of rhythm.

when these groups had existed 45 minutes, extra-systoles intervened between the groups. It is well-known, that these occur by preference in greater pauses.

Halving of the rhythm has not been attained with this heart; most likely it would have occurred, if the poisoning had made greater progress. So I often saw *p*-bigeminus as a transition from the normal rhythm into the halved one and in transitions of rhythms (vide Fig. 6).

Here we see in the upper-row of curves (20 min. after the injection of 4 drops of 1% veratrine) bigeminus-groups pass into the normal rhythm; 5 minutes before the bigeminus-groups the rhythm was halved; in the next row (5 min. later) we have again bigeminus-groups, and 15 min. after this (3<sup>rd</sup> row) the rhythm is halved

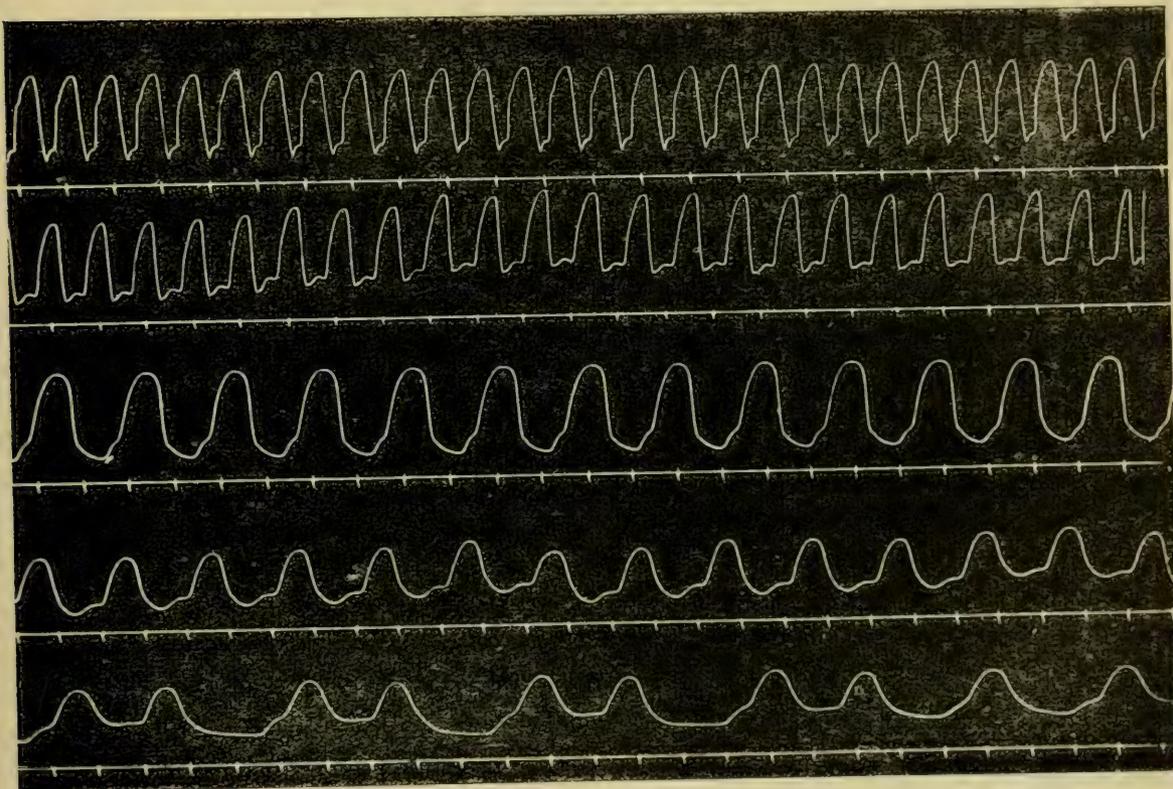


Fig. 7.

First row: Suspension-curves of the unpoisoned frog's heart; 2nd 10 min. after the injection of 10 drops of 1% aect. veratrin; 3rd row: 5 min. later halving of the rhythm; 4th row: 10 min. after row 3, the systoles of the halved rhythm grow smaller; 5th row: 5 min. after row 4, bigeminus-groups. These groups develop themselves because each 3rd and each 2nd systole of the normal rhythm are represented; in the latter part of this row every 3rd systole can twice be observed. The bigeminus groups form here a transition between the halved rhythm and the rhythm, of which every 3rd systole of the rhythm shows itself.

again. The duration of 3 periods of this halved stage is equal to the duration of 2 bigeminus-groups. The distance between 2 auricles in one group is 2 sec., the duration from the 2<sup>nd</sup> to the first of the following group is  $2\frac{1}{2}$  sec. This teaches us how great the retardation can be in the connection-systems between the sinus venosus and the auricle.

*P*-bigeminus does not only occur as transition with halving of rhythm, but likewise as transition between the halved rhythm and a still slower rhythm.

Fig. 7 is an example of this phenomenon. The upper-row gives the curves before the injection. The 2<sup>nd</sup> row of curves is represented 10 min. after the injection of 10 drops of veratrine into the abdominal cavity. In the 3<sup>rd</sup> row (represented 5 min. after the 2<sup>nd</sup>) the rhythm is halved. The same stage exists still in the 4<sup>th</sup> row, but the systoles have become smaller, the *a-v*-interval has increased a second time (in the halved rhythm of row 3 the lengthened *a-v*-interval was reduced again). In the 5<sup>th</sup> row the systoles are ranged in bigeminus-groups. Measurement shows us that from the normal rhythm after the first systole of each group one systole, after the 2<sup>nd</sup> systole 2 systoles, are missing.

Here we have consequently a bigeminus of which alternately every 3<sup>rd</sup> and every 2<sup>nd</sup> systole are expressed. This bigeminus also is again a transition into a slower rhythm. The last 2 systoles of this row indicate this rhythm. Here every 3<sup>rd</sup> systole is every time expressed.

With unpoisoned frog's hearts heart-bigeminy occurs also frequently as transition with halving and variation of rhythm. Thus I have a series of curves of a suspended normal frog's heart, on which first groups of 8, 10, 4, and 3 were formed; afterwards bigeminy took place, which was converted into the halved rhythm.

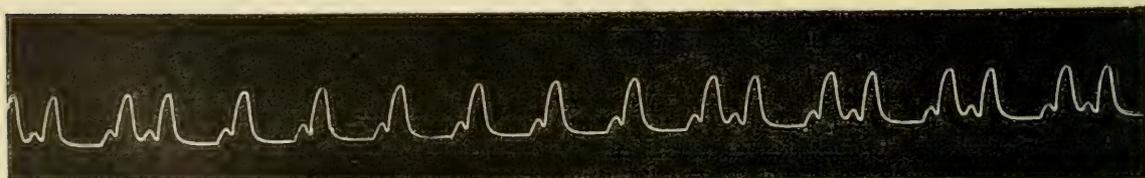


Fig. 8.

Bigeminus-groups — halved rhythm — bigeminus-groups.

This halved rhythm was afterwards converted again into heart-bigeminy. These last 2 transitions are represented in Fig. 8. Two of the bigeminus-groups answer to 3 systoles of the halved rhythm.

By measurement we can easily discover the important retardation in the conducting-systems between the partitions of the heart for every 2<sup>nd</sup> systole of the groups.

In all the cases of heart-bigeminy mentioned here we have before us a heart, pulsating in 2 rhythms. The first systole of each group, which is preceded by a longer pause, is of the type of a slower rhythm, the 2<sup>nd</sup> systole is of a quicker rhythm. Each group has one systole out of each of the 2 rhythms, between which the bigeminy occurs as a transition.

In every bigeminus-group the first systole is wider than the 2<sup>nd</sup>; what is wanting in the 2<sup>nd</sup> systole after the shorter pause, is added again to the first systole after the longer pause (law of the conservation of energy of the heart). The same relation we found in the velocity of the conduct in the connection-systems between the partitions of the heart for the two systoles of the bigeminusgroups. In my former communication I called already the attention to this fact.

Likewise in another way I saw heart-bigeminy occur after poisoning with veratrine. In the still normal rhythm the conduct in the connection-systems of the partitions of the heart can be alternately retarded. This is the origin of bigeminus-groups. Fig. 9 represents an example.

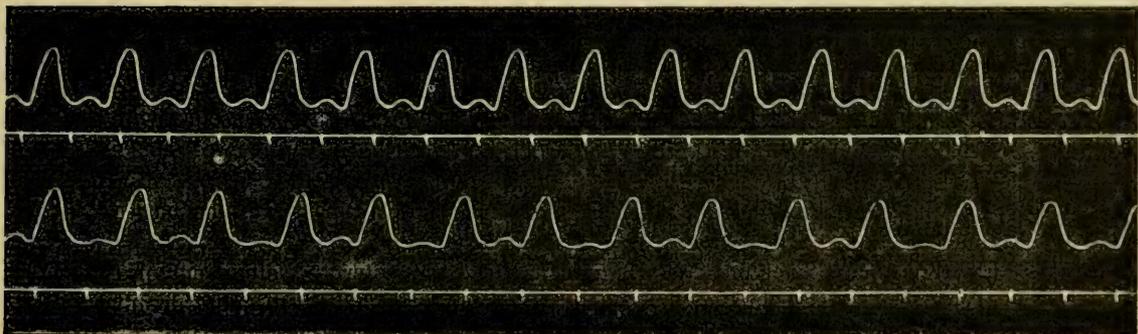


Fig. 9.

The lower row of curves shows bigeminus-groups caused by alternating lengthening of the *a-v*-interval.

In the 2<sup>nd</sup> row of curves we see every second *a-v*-interval retarded: the auricle-systoles for these heart-periods have diminished. I found still a third cause for the occurrence of heart-bigeminy in the hearts of my frogs that were poisoned with veratrine. Up till now I found this sort of heart-bigeminy only once. In fig. 10 in the upper row we find them represented. I represented this row about 15 min. after the injection of 8 drops of 1<sup>o</sup>/<sub>10</sub> veratrine. Each curve of this row

is an extra-systole of both ventricle and auricle at the same time (the irritation originated thus evidently in the connection-systems of these two partitions of the heart). The pauses between the first 5 curves are equal in length. Then we obtain alternately longer pauses, whilst between these longer pauses again normal ones occur (normal at least for this row of extra-systoles). So bigeminus-groups develop themselves, the two curves of which consist of extra-systoles of ventricle and auricle at the same time. It is evident that here the connection-systems between the sinus venosus and the auricle are

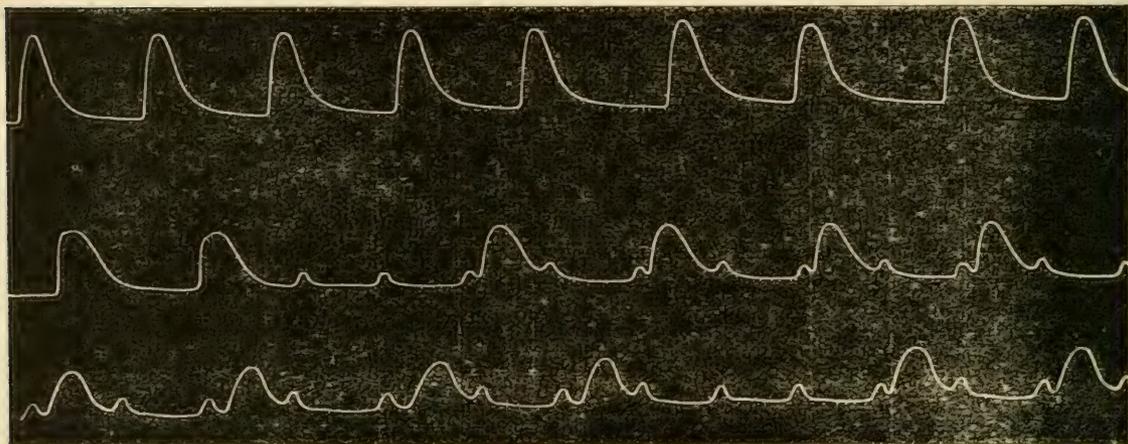


Fig. 10.

Upper row: Extrasystoles of ventricle and auricle in frog's heart poisoned with veratrine after blocking of the *si-a* connecting systems. The curves range themselves from the sixth curve in bigeminus-groups.

2nd row: Cessation of the heart-blockade, the ventricle pulsates in the halved rhythm.

3rd row: Increase of the *a-v*-interval of curve 1—4; after the falling out of 1 ventricle-systole shortening of the *a-v*-interval, which is lengthened again already in the following curve.

blockaded. It is difficult to explain the cause why the extra-systoles range themselves here in bigeminus-groups. In the 2<sup>nd</sup> row we see still 2 extra-systoles, after which suddenly the separate auricle- and ventricle-systoles appear again. The ventricle pulsates in the halved rhythm. The auricle-rhythm is much quicker than that of the extra-systoles. This is an affirmation of the well known fact that the peculiar rhythm for auricle and ventricle is much less frequent than the rhythm that originates in the sinus venosus (2<sup>nd</sup> STANNIUS ligature). The lower row of curves shows again a lengthening *a-v*-interval, till the 5<sup>th</sup> ventricle-systole falls out; for the next-following heart-

period the *a-v*-interval is again much shortened, in the then following period it lengthens again.

We found thus, that heart-bigeminy after poisoning with veratrine can develop itself in 3 ways.

1. as transition-stage between the normal rhythm and the halved one;
2. by alternating retardation in the conduct-systems between the different heart-partitions.
3. with accumulations of extra-systoles after blockading of the connection-systems between sinus venosus and atrium. I found the manner of development as it is indicated by HERRING only in disconnected groups. I never found a row of bigeminus-groups of which every 2<sup>nd</sup> systole was an extra-systole.

**Geophysics.** — *On the relation between departures from the normal in the strength of the trade-winds of the Atlantic Ocean and those in the waterlevel and temperature in the northern European seas.* By P. H. GALLÉ. (Communicated by Dr. J. P. VAN DER STOK).

(Communicated in the meeting of February 27, 1915).

1. From hydrodynamical and oceanographical investigations in the North-Sea, the Baltic, the Norwegian and the Barents-Sea, the existence of the following phenomena is evident.

*a.* Mean values from Dutch<sup>1)</sup>, Norwegian<sup>2)</sup>, German<sup>3)</sup> and Finnish<sup>4)</sup> tide-gauges show an annual periodicity in the waterlevel of the North-Sea and the Baltic, displaying a minimum in spring, a maximum and secondary-maximum — separated by a rather clearly indicated secondary-minimum — in autumn.

*b.* Temperature and salinity observations of the underlayers in the North-Sea<sup>5)</sup>, the Norwegian<sup>6)</sup> and the Barents-Sea<sup>6)</sup>, show a periodicity

<sup>1)</sup> Koninklijk Nederlandsch Meteorologisch Instituut N<sup>o</sup>. 90.

J. P. VAN DER STOK. Etudes des phénomènes de marée sur les côtes néerlandaises.

1. Analyse des mouvements périodiques et apériodiques du niveau de la mer, 1904.

<sup>2)</sup> H. GEELMUYDEN. Resultater af Vandstands Observationer paa den Norske Kyst. Hefte VI, 1904.

<sup>3)</sup> OTTO PETERSSON. Ueber die Wahrscheinlichkeit von periodischen und unperiodischen Schwankungen in dem Atlantischen Strome und ihren Beziehungen zu meteorologischen und biologischen Phaenomenen. Rapports et Procès Verbaux du Conseil Permanent pour l'Exploration de la mer. Vol. III, 1905.

<sup>4)</sup> ROLF WITTING. Finländische Hydrographische-Biologische Untersuchungen N<sup>o</sup>. 7, Helsingfors 1912.

<sup>5)</sup> Report on Norwegian Fishery and Marine-Investigations Vol. II, 1909, N<sup>o</sup>. 2. The Norwegian Sea, its physical oceanography, based upon the Norwegian Researches 1900—1904 by BJÖRN HELLAND—HANSEN and FRIDTJOF NANSEN.

<sup>6)</sup> L. BREITFUSZ. Oceanographische Studien über das Barentsmeer. Petermanns Geogr. Mitth. 1904 Heft II.

of the same kind; a minimum in spring, a corresponding maximum in autumn.

To explain the phenomenon, whose generality has become known only of late years, different ways have been tried.

In the supposition that it was limited to the southern part of the North-Sea and the Baltic and thinking the wind responsible for the periodical fluctuations VAN DER STOK comes to the following conclusion.<sup>1)</sup>

“A comparison of these (wind) results with those, indicating the periodical and non-periodical fluctuation of the sealevel shows, that — though some correspondency as the distinct November-minima cannot be denied — a real connection fails. Neither the April-minimum, nor the October-maximum can be explained as a result of the wind on our coast.

A more accurate investigation of the fluctuations in the waterlevel as well as of those in the windsystem both on the Dutch coast and the whole North-Sea is desirable.”

GEELMUYDEN says:

“The yearly fluctuation is very marked along the whole Norwegian coast; I think an explanation must be looked for in periodical changes of pressure and wind.”

In PETTERSON'S work the following quotation is to be found:

“If on the other hand, only Dutch observations had been accessible, the inferences drawn from them would certainly have pointed to the wind as the originator of the fluctuations. Now, since a comparison of facts has shown the analogy of the fluctuations in the North-sea, the Baltic and the Kattegat, such inferior explanations are excluded, and we must acknowledge the fluctuations to be the outcome of a general pulsation of the ocean from the tropics to the Polar Sea. The pulsation of the northern seas is analogous with that of the Atlantic.”

Speaking about the North-Atlantic Current it is evident he considers that stream not to be a direct offshoot of the Gulfstream, an opinion not generally shared.

WITTING after having pointed out the correspondency of phenomena in North-Sea and Baltic, tries to find an explanation in fluctuations in the quantity of water in these seas. In his opinion these fluctuations are caused by the wind, however not by the wind in the North-Sea or in the Baltic, but so far as the Baltic is concerned by the wind near its gates; the Skager Rak, the Belts and the Kattegat.

BREITFUSZ found from serial-observations in latitude 71° N. and

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<sup>1)</sup> l. c. p. 20.

longitude  $33^{\circ}5$  E. that from June till November the temperature as well as the salinity of the whole watermass increased and especially in the deeper layers. The velocity of the current also increased in this period; we have to do here with the Northcape-current, one of the outer ramifications of the Gulfstream. After discussing this increase BREITFUSZ continues:

“Not in local conditions we should look for the origin of these fluctuations, but in the Gulfstream and in the many causes that modify the stream on its way, thousands of miles long, from its cradle under the Equator, through the Caribbean Sea and the Atlantic to the Polar regions.

2. In our opinion fluctuations in the intensity of the Gulfstream are the cause of the fluctuations in the waterlevel and we were strengthened in this opinion, when we learned from BREITFUSZ's investigations the general nature of this phenomenon.

But if fluctuations in the Gulfstream are responsible, then it must be possible to detect a similar periodicity in the North- and South-Equatorial current and in the North- and South-East trades.

We calculated the monthly mean values and departures from

TABLE I.

	Number of days with observations	Current 1855—1900			Wind 1855—1914		
		Direction	Miles in 24 h.	Departure	Direction	Meters p. sec.	Departure
January	1393	N $281^{\circ}$ E.	4.95	-1.27	N $64^{\circ}$ E.	5.46	+0.26
February	1161	285	4.41	-1.81	62	5.17	-0.03
March	1398	282	5.05	-1.17	63	4.65	-0.55
April	1138	282	5.34	-0.88	62	4.69	-0.51
May	1425	285	5.89	-0.33	60	5.76	+0.56
June	1250	278	6.97	+0.75	59	6.25	+1.05
July	1411	272	8.90	+2.68	56	6.12	+0.92
August	1265	267	7.50	+1.28	56	5.28	+0.08
September	1114	268	7.84	+1.62	61	5.28	+0.08
October	1098	270	6.71	+0.49	67	4.54	-0.66
November	1096	269	6.17	-0.05	64	4.55	-0.65
December	1411	273	4.90	-1.32	68	4.71	-0.49

yearly mean values for the region  $15^{\circ}$ — $25^{\circ}$  N. and  $25^{\circ}$ — $40^{\circ}$  W., as given in the preceding table <sup>1)</sup>).

For the South-Atlantic monthly data are not at our disposition, below we give the three-monthly mean values and departures from the normal for the region  $5^{\circ}$ — $10^{\circ}$  S. and  $15^{\circ}$ — $35^{\circ}$  W. <sup>2)</sup>).

TABLE II.

	Direction	m. p. sec.	Departure
Dec.—Febr.	N $123^{\circ}$ E.	4.58	— 0.56
March—May	117	4.29	— 0.85
June—Aug.	132	6.12	+ 0.98
Sept.—Nov.	137	5.58	+ 0.44

Maxima and minima of the North-East and South-East trades appear to coincide fairly well, table I shows a real correspondency between the North-East trade and the North-Equatorial current; the positive and negative departures in the strength of the trade wind correspond with one exception with those in the velocity of the Equatorial current and show a difference in phase of one month. We should keep in mind, that winds with great stability as the trades and monsoons are generally considered to be the prime current-generators; furtheron in this study we will try to explain departures from normal-level in the North-Sea or from the normal-surface of open water in the Barents-Sea, with the aid of fluctuations in the strength of the North-East trade.

It would be better for this purpose to make use of fluctuations in the North-Equatorial current, but as a matter of fact current-observations are always less in number than windobservations and therefore we have to rely on the wind.

In the following table we give the monthly departures from the yearly mean level, as they have been calculated from long tide-gauge-observations at 7 Baltic and 3 North-Sea stations; Fig. 1 shows the departures in velocity of the stream and in the waterlevel.

<sup>1)</sup> Kon. Ned. Met. Instituut.

N<sup>o</sup>. 95. Observations océanographiques et météorologiques dans la région du courant de Guinée 1855—1900. Utrecht 1904.

N<sup>o</sup>. 107. Monthly Meteorological Data for ten-degree squares in the Atlantic and Indian Oceans 1900—1914.

<sup>2)</sup> Pilot Chart of the South Atlantic Ocean. Dec.—Jan.—Febr. etc. Hydrographic Office and Weather Bureau Washington D. C.

The correspondency is considerable, in spring we have a phase-difference of two months, in autumn of three, it stands to reason that either phase-difference can be  $2\frac{1}{2}$  months.

TABLE III.

Monthly departures in waterlevel in cm.											
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
-2.5	-4.0	-5.8	-9.0	-6.7	-3.1	+3.4	+5.7	+6.7	+8.6	+1.7	+5.6

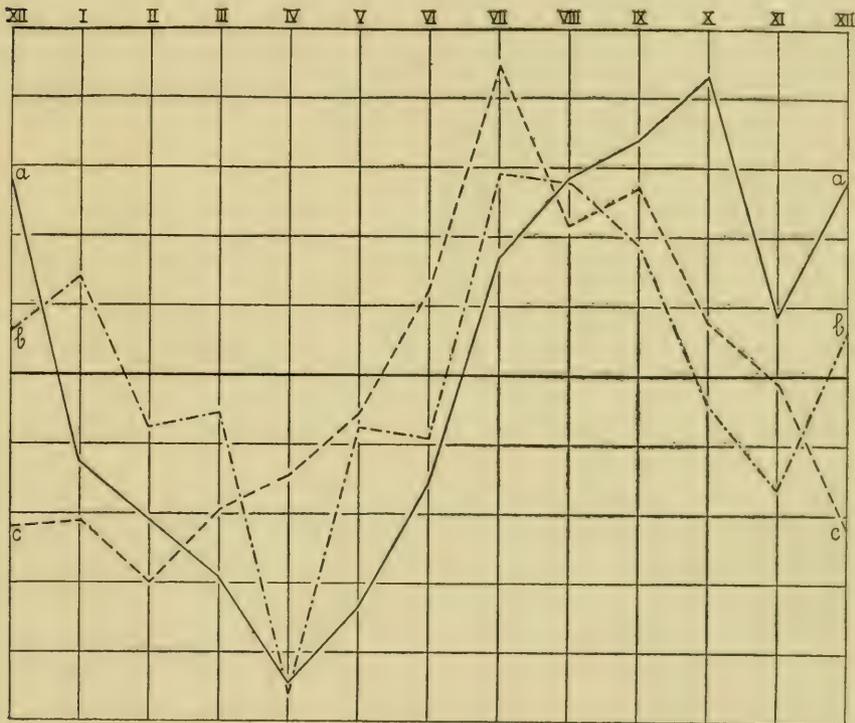


Fig. 1.

*a.* Waterlevel North-Sea and Baltic. *b.* Raising-power North-Sea-wind.  
*c.* Equatorial Current.

It is evident from the above:

1<sup>st</sup>. Monthly fluctuations in the velocity of the North-Equatorial current (or in the strength of the North-East trade) are responsible for monthly fluctuations of the waterlevel in the North-Sea and the Baltic.

2<sup>nd</sup>. The two groups of fluctuations show a phasedifference of 2 or 3 months.

3<sup>rd</sup>. The origin of the Gulfstream lies under the Equator, the North-Atlantic current is a direct offshoot of the Gulfstream and is the connection between the Gulfstream proper and the North-Sea, the Baltic, the Norwegian and the Barents-Sea.

4<sup>th</sup>. BREITFUSZ was in 1904 the first to point out the direction in which we had to look for the solution of this problem.

3. We mentioned before that VAN DER STOK and WITTING thought the water-raising power of the local wind or of that near the entrances of the North-Sea and the Baltic responsible for the fluctuations in the waterlevel.

We do not know how WITTING proceeded; from mean monthly windresultants, as calculated but not published by VAN DER STOK for Swambister, Bergen, Skudenes, Helder and Flushing, we derived a mean monthly "North-Sea-wind" (Table IV).

TABLE IV.

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Direction	206°	207	220	278	314	321	282	256	235	216	196	199
M. p. s.	2.69	2.15	1.88	0.58	1.80	1.90	2.05	2.03	2.06	1.99	2.42	2.86

The first thing necessary to cause a rise of the waterlevel on a coast is a motion of the water or a current perpendicular to that coast. The direction of the Dutch, Danish, and Norwegian coast is about SSW—NNE; a maximum rise of the water will be caused by an ESE-ly current. WITTING has shown that between wind and winddrift in inland seas as the Baltic, a difference in direction exists of 25° to the right (southern latitude to the left); the most favourable winddirection to cause a rise of the water, is in our case N 268° E.

In order to judge of the waterraising-power of the different monthly windresultants of table IV we project them on the direction N 268° E. and consider the squares of the projections; we get the following monthly values and departures from the mean (Table V *b* Fig. 1).

The minima in spring and autumn in waterlevel and raising-power coincide; the maximum raising-power between July and August is

TABLE V.

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
3.34	2.24	2.36	0.33	2.25	2.17	4.07	4.03	3.56	2.43	1.81	2.93
+0.72	-0.38	-0.26	-2.29	-0.37	-0.45	+1.45	+1.41	+0.94	-0.19	-0.81	+0.31

followed by a maximum in level in October, the December-level-maximum nearly coincides with the maximum in raising-power of the wind between December and January.

We also calculated the raising-power of the monthly windresultants and their departures from the normal (*b*) alone for the Dutch coast (Table VI); Fig. 2 shows them with the departures in waterlevel (*a*) on the Dutch coast and those in the Equatorial current (*c*).

TABLE VI.

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
<i>a</i> -1.4 cM.	-7.0	-5.8	-9.7	-6.1	-4.2	+1.3	+4.6	+6.0	+12.1	+2.6	+7.7
<i>b</i> -0.31	-0.42	+0.11	-2.87	-3.60	-0.43	+1.87	+3.66	+1.89	+0.21	-1.86	+0.82

The correspondency between the different curves has become clearer and we cannot doubt any longer that besides fluctuations in the velocity of the Equatorial current, monthly fluctuations in the waterraising-power of the wind are responsible for periodical fluctuations in the waterlevel of the North-Sea and adjoining seas.

The question is raised:

“Is it possible to express numerically the relation between fluctuations in waterlevel in the North-Sea and in the Baltic and fluctuations in the trade-winds and waterraising-power of the wind on our coast?”

We have already pointed to the fact that for the solution of this question we had to consider the Equatorial current or trade-wind for an earlier period as that relative to the waterlevel.

In our opinion the waterlevel of 1914 is governed by the Equatorial current November 1913—October 1914. The correlationfactor between fluctuations in waterlevel and trade-wind is 0.66.

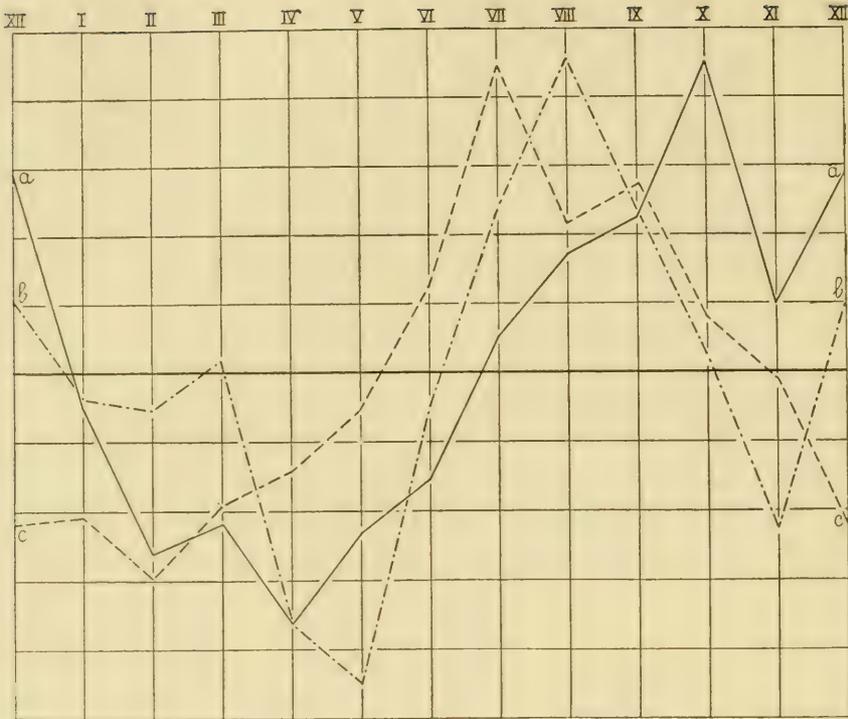


Fig. 2.

a. Waterlevel Dutch coast.    b. Raising-power wind Dutch coast.  
c. Equatorial Current.

The correlation between waterlevel, trade-wind and water-raising power is 0.82.

If it were possible to make a trustworthy prognostication about the "North-Sea wind", we should be able to forecast with a fair certainty the level to be expected, for during two years we have known fairly well the behaviour of the trade winds from month to month,<sup>1)</sup> a progress made by international coöperation on VAN DER STOK'S instigation.

The correlation between fluctuations in the Equatorial current and the waterlevel is far greater viz. 0.85. It will be tried to secure current observations in time in sufficient quantity, for in our opinion

<sup>1)</sup> Kon. Ned. Meteor. Instituut 107<sup>A</sup> and 107. Monthly Meteorological Data for ten-degree squares in the Atlantic and Indian Oceans.

107<sup>A</sup> Computed by the Royal Netherlands Meteorological Institute from Swedish and Dutch Observations 1900—1912 and from international observations January—June 1913.

107 Computed by the Royal Netherlands Meteorological Institute from international logs and observations 1<sup>1</sup> January—June 1913, 1<sup>2</sup> July—December 1913, Utrecht 1914.

the solution of some meteorological and biological problems is closely connected with a more accurate knowledge of the watertransport through the ocean to our shores.

GEELMUYDEN found that along the Norwegian coast the behaviour of the waterlevel was the same as along the more southern shores in question; from the constants he gave for the partial tide  $S_a$ , it was however not possible to conclude anything about the existence of a November-secondary-minimum.

In the North of Norway the maximum falls later than in the South; the reason why, may perhaps be found, by comparison of table VI with the following table, where we calculated the departures from the average (1893—1913) of the water-raising power of the wind for Bödö.

TABLE VII.

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
+0.24	-1.99	-2.56	-0.30	+1.41	+2.17	+2.57	+1.59	+1.88	+0.57	+0.47	+6.11

4. In the preceding pages we think we have demonstrated that — at least for a rather great number of years — monthly fluctuations in the waterlevel in the North-Sea and the Baltic and halfyearly fluctuations in temperature and salinity in the Barents-Sea are originated by monthly fluctuations in the velocity of the Equatorial current or strength of the North-East trade in the North-Atlantic in connection with the water-raising power of the wind in the neighbourhood.

The question arises — and with this we come to the direct application of the preceding theory — is it possible now, to say something definite about future fluctuations in meteorological or oceanographical elements in one of the Northern Seas.

We told already, why we had — by way of introduction at least — to make use of fluctuations in the North-East trade and that the effect of these fluctuations was felt after about two or three months in the northern European Seas.

We give the following examples.

PETTERSSON has found that between Thorshavn and Iceland from August 1902—August 1903 the water of Atlantic origin lost 131 Kilogram-calories daily, from August 1903—August 1904 the daily gain was 230 calories.

We have to calculate the mean strength of the trade from June 1902—1903 and 1903—1904 and find N 78° E., 2.07 and N 69° E.

3.26 BEAUFORT-units; the average annual strength is N 70° E. 2.85. These values agree with the above-mentioned figures of loss and gain of heat.

A second series of data to justify our theory we find in HELLAND-HANSEN'S and NANSEN'S wellknown work <sup>1)</sup>, where the following figures for the open water in the Barents-Sea for May are given in thousands of square kilometers.

TABLE VIII.

May	1900	1901	1902	1903	1904	1905	1906	1907	1908
Thousands of □ kilometers	440	398	249	469	696	639	576	645	568

In NANSEN'S opinion, the surface of open water depends in a great measure upon the watertemperature of the preceding winter. According to this we have only to compare the strength of the trade with these figures, keeping in mind that departures from the mean surface of open water in May 1900 should be in accordance with departures from the mean strength of the trade-wind for the period Sept. or Oct. 1898—Sept. or Oct. 1899.

In table IX we give the corresponding departures, the correlation is 0.55.

TABEL IX.

1900	1901	1902	1903	1904	1905	1906	1907	1908
-0.28	-0.43	-0.12	-0.13	-0.10	+0.53	+0.22	+0.03	+0.28
-80	-122	-271	-51	+176	+119	+56	+125	+48

Lastly we will consider the relation between the departures from the mean value of the annual North-sea level on the Dutch coast <sup>2)</sup> and those in the mean average strength of the trade, in such a way that the windyyear ends consecutively 31<sup>st</sup> August, 30<sup>th</sup> September etc.; the wateryear always on 31<sup>st</sup> December. In table X it is evident that a difference in time of two months gives the best

<sup>1)</sup> The Norwegian Sea. Its physical oceanography based upon the Norwegian researches 1900—1904 by BJÖRN HELLAND HANSEN and FRIDTJOF NANSEN. Report on Norwegian Fishery and Marine Investigations, Vol. II 1909. N<sup>o</sup>. 2.

<sup>2)</sup> The data required for this purpose we owe to the service of the "Rijks-Waterstaat".

correlation; in Fig. 3 the curves representing the departures in water level (*b*) and strength of the trade (*a*) are given.

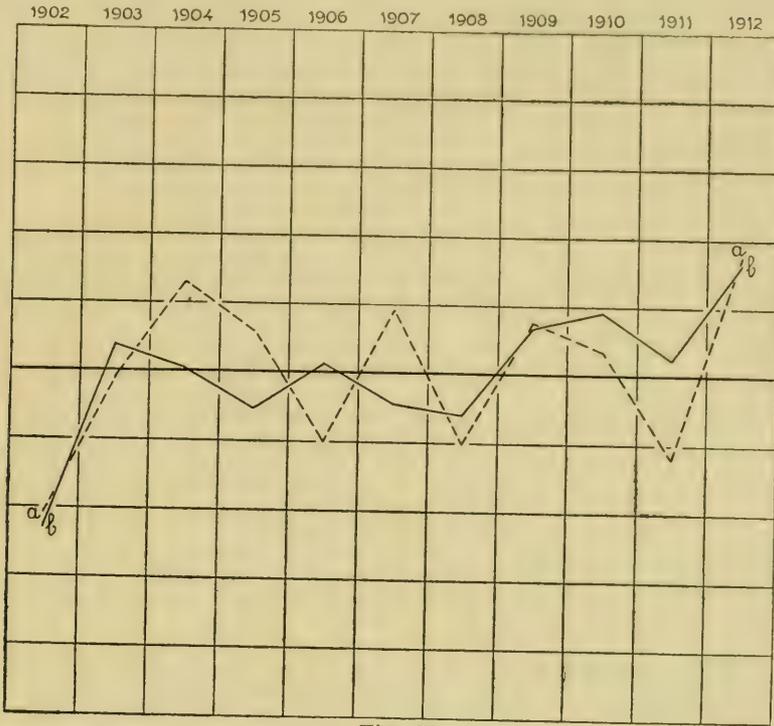


Fig. 3.

TABLE X.

1902	1903	1904	1905	1906	1907	1908	1909	1910	1911	1912		Corr.
-92 mM.	+15	+1	-23	+4	-18	-23	+27	+37	+9	+65		
-0.18	-0.34	+0.40	+0.08	-0.12	+0.14	-0.03	+0.04	+0.10	-0.27	+0.17	Aug.	0.24
-0.38	-0.16	+0.35	+0.05	-0.12	+0.13	-0.07	+0.07	+0.11	-0.30	+0.25	Sept.	0.55
-0.42	-0.02	+0.26	+0.12	-0.20	+0.19	-0.20	+0.14	+0.08	-0.24	+0.34	Oct.	0.65
-0.45	-0.16	+0.28	+0.22	-0.25	+0.38	-0.46	+0.28	-0.07	+0.02	+0.21	Nov.	0.46
-0.42	-0.04	+0.19	+0.18	-0.18	+0.32	-0.46	-0.02	+0.17	-0.08	+0.34	Dec.	0.59

The answer to the question put in the beginning of this chapter, is therefore, that when we have to do with somewhat important

departures from the average in the strength of the North-East trade, it seems possible to us, to make a forecast about the sign of the departure from the normal of some phenomena in the Northern European seas.

Whether the correlation will prove to be greater or smaller if longer series are at our disposition, cannot be said with any certainty beforehand.

**Chemistry.** — “*The connexion between the limit value and the concentration of Arsenic Trisulphide sols*”. By Dr. H. R. KRUYT and JAC. VAN DER SPEK. (Communicated by Prof. E. COHEN).

(Communicated in the meeting of February 27, 1915).

1. When one of us<sup>1)</sup> carried out experiments with the  $As_2S_3$  sol conjointly with C. F. VAN DUIN, it once struck us that a sol, which we had diluted to half its concentration, had retained nearly the same limit value. The object of the investigation communicated here was to endeavour to get some more knowledge as to the connexion between the  $As_2S_3$  concentration and the limit value of the sol.

2. One may preconceive an idea as to this connexion. We assume for the moment that the sols differ only in concentration but not in the size of their particles. Now the limit value  $\gamma$  is the concentration at which so much of the coagulating cation is withdrawn by adsorption that the charge of the particles is diminished to a definite value differing but little from 0. Hence, the adsorbed quantity of cation ( $a$ ) per particle is characteristic of the limit value. This again is connected with the concentration  $\chi$  in cation in the solution after the conglutination<sup>2)</sup> according to this equation:

$$a = k\chi^{\frac{1}{n}}$$

so that  $\chi$  is, therefore, also characteristic of the limit value *but independent of the concentration of the sol*. As for the limit value  $\gamma$  we simply take into account the bruto-added electrolyte quantity,  $\gamma$  is as a rule not independent of the concentration.

In the Fig. 1 and 2 are represented schematically two sols in which the second has the double concentration of the first. When properly choosing the units we have in Fig. 1:  $\gamma_1 = \chi + a$ , in Fig. 2:  $\gamma_2 = \chi + 2a$ .

<sup>1)</sup> KRUYT and VAN DUIN, Koll. Beih. 5, 269 (1914).

<sup>2)</sup> For fuller details compare KRUYT, Proc. 17, 623 (1914).

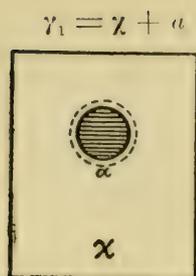


Fig. 1.

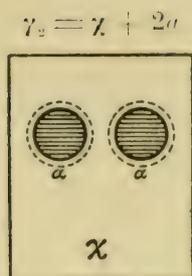


Fig. 2.

It will now be evident without any further comment that the limit value is not (or but very faintly so) a function of the concentration when  $a$  is small in regard to  $\gamma$  and when consequently  $\gamma = \chi$ . In the case of monovalent cations with their relatively high limit value this will have to be the case. In the di-, and still in a higher degree in the trivalent cations, the limit value will have to increase with the concentration.

3. Concentrated sols of  $\text{As}_2\text{S}_3$  were made according to a method devised by SCHULZE<sup>1)</sup>. After in a nearly saturated solution of  $\text{As}_2\text{O}_3$  this had been converted into  $\text{As}_2\text{S}_3$ , a fresh quantity of  $\text{As}_2\text{O}_3$  was dissolved and  $\text{H}_2\text{S}$  again passed through. This treatment was then repeated a few times<sup>2)</sup>. The determination of the limit value for such concentrated sols must be modified somewhat. A mere shaking of the glasses is not sufficient as after the conglomeration, they may be placed upside down without anything running out. Hence, before and after the two hours required, stirring rods were used. In the case of monovalent cations the precipitate obstinately adheres to the glass walls thus rendering the observation much more difficult.

In the first five columns of the subjoined table 1 are communicated the results of a series of measurements. The determinations have been carried out with the same measuring instruments, standard solutions, working arrangements, in fact as much as possible under the same conditions. For each concentration a separate sol was prepared.

The concentration was determined by precipitating the  $\text{As}_2\text{S}_3$  with  $\text{HCl}$ , drying on a Gooch filter at  $80^\circ$  and weighing.

In Table 1 all concentrations are *end* concentrations, that is they relate to the volume after addition of the electrolyte solution.

In Fig. 3 these results are represented in such a manner that the limit value of experiment 1 is put for each electrolyte each time as

<sup>1)</sup> Journ. f. prakt. Chem. N. F. 25, 431 (1882).

<sup>2)</sup> Full experimental details will be published elsewhere.

TABLE 1.

No.	gr. $\text{As}_2\text{S}_3$ per K.G. Sol	Limit value			Number of particles		
		KCl	BaCl <sub>2</sub>	AlK[SO <sub>4</sub> ] <sub>2</sub>	Dilution used	20 times the number	Number calcul- ated for 1:2000
1)	5	56	0.99	0.183	—	—	—
2	18.0	69	1.20	0.291	$2 \cdot 10^4$	38	19
3	42.8	50	1.92	0.540	$1 \cdot 10^5$	22	55
4	74.7	59	2.87	0.649	$2 \cdot 10^5$	37	185

1) No. 1 is borrowed from the investigation of KRUYT and VAN DUIN, loc.cit. Table X.

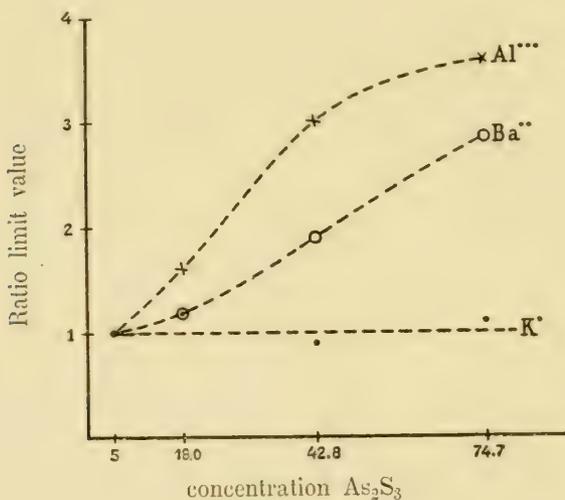


Fig. 3.

1.00. From this we notice how the *results completely confirm the correctness of the train of thoughts of the previous paragraph*. To the less regular course with the monovalent cation we will refer presently.

4. We desired to get some insight whether our premise that the dispersity degree of our sols was still the same, had proved satisfactory. Direct determinations of the dispersity degree have been carried out by ZSIGMONDY<sup>1)</sup> with gold sols, by WIEGNER<sup>2)</sup> with oil

<sup>1)</sup> Ann. de Phys. [4] **10** 16 (1903).

<sup>2)</sup> Koll. Beih. **2** 213 (1911).

emulsions. For that purpose are counted in the ultramicroscope the number of particles in a definite volume-element. We have also done this with the ultra microscope (source of light self-regulating arc lamp according to WEULE, width of aperture 5, objective ZEISS D\*, compensation ocular 18, length of cylinder 16, EHRLICH's screen 17). Dilutions were made in such a manner that never more than five particles were simultaneously present in the field of vision. In consequence of the BROWNIAN movement the mean from a number of observations had to be taken. Generally a series of 20 observations was made four times. Below in Table 2 the list of the observations of one sol (N<sup>o</sup>. 2) is given; for the other sols the end results are given in Table 1.

TABLE 2.

2 1 1 2	2 2 2 1	1 1 2 3	1 2 3 1
2 2 2 1	2 1 3 2	3 2 2 3	2 1 2 2
2 2 2 2	2 2 1 2	2 2 3 3	1 1 3 4
3 3 3 1	1 2 1 3	3 1 2 0	1 2 2 2
2 1 2 2	1 1 2 2	1 2 1 2	2 3 3 1
total 38	total 35	total 39	total 39
general average of 20 measurements 38			

These results cannot be interpreted in the same manner as those relating to gold sols. For there we see the luminous particles against a completely dark background. Here on the other hand we notice besides the particles an undistinguishable pale blue illumination of the field. We therefore have particles of unequal size in the sol and we *only count the large particles*. If now at the different concentrations all was equal, we ought, on recalculating our results to one standard solution, to find figures which increase proportionally with the concentration. Such figures are found in the last column of Table 1; they are so chosen that the concentration and standard figure in experiment 2 are about equal. We now see at once that the number of large particles increases more rapidly than the concentration, therefore, the concentrated sols possess probably a smaller average dispersity degree than the diluted ones. This can be readily understood because the repeated boiling, in order to dissolve fresh  $As_2O_3$ , probably leads to enlargement of the particles.

Nevertheless this result does not diminish the value of our con-

firmatory experiment. Just the reverse; with a *lesser* dispersity corresponds a *lower* limit value. Hence, if the dispersity had been the same in all these experiments the difference between the K', Ba'' and Al'''-ion would have been still more pronounced.

5. In order to completely exclude meanwhile the complication of the difference in dispersity degree we have still made another series of experiments. We have prepared a large quantity of a concentrated sol and from this made by dilution with water three sols of different concentration. Of these four sols which thus were derived from the same original liquid and exhibit undoubtedly<sup>1)</sup> the same average size of particles, we have again determined the value limits with KCl, BaCl<sub>2</sub> and AlK(SO<sub>4</sub>)<sub>2</sub>. To eliminate all differences which might occur owing to the duration of the experiment all determinations have been made within 38 hours. Table 3 shows the result:

TABLE 3.

No.	gr. As <sub>2</sub> S <sub>3</sub> per K.G. sol	Limit value		
		KCl	BaCl <sub>2</sub>	AlK(SO <sub>4</sub> ) <sub>2</sub>
1	5	81	1.35	0.106
2	25	61	1.79	0.266
3	36	56	2.11	0.350
4	50	53	2.53	0.442

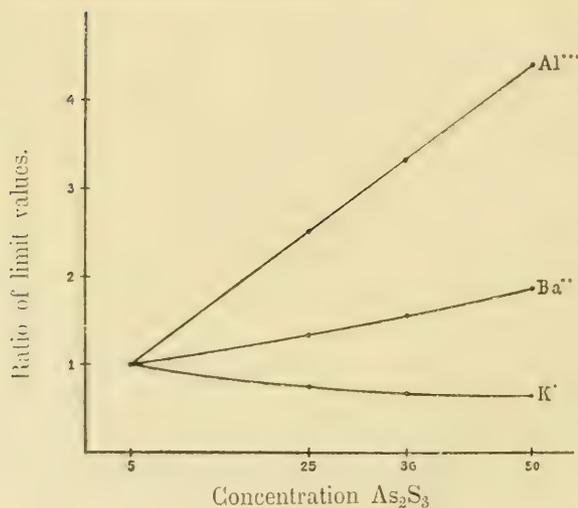


Fig. 4.

<sup>1)</sup> It cannot be denied with absolute certainty that the dilution may exert an influence on the size of the particles, but even if such an influence does exist it is certainly of a lower order.

In Fig. 4 the results are again represented graphically with the limit value of the sol N<sup>o</sup>. 1 as unit. The result agrees well with what was expected, only the limit values for K. exhibit an unmistakable depression with increasing sulphide concentration. We must for the present refrain from trying to explain this remarkable anomaly.

6. The experience gained during the above described research has given rise to a number of questions; fresh experimental series started with the intention of answering those had to be postponed on account of the present circumstances. Hence, we can only point to some provisional results.

We feel convinced that on boiling an As<sub>2</sub>S<sub>3</sub> sol an enlargement of the particles really takes place (light absorption, ultramicroscopic image, depression of the limit value of the Al<sup>+++</sup>-ion). At the same time it appeared that, on boiling, the particles do not become enlarged equally, but that the boiled sol contains particles of all sizes and that *a fractional precipitation seems possible*. This fact has, up to the present, only been recorded in the case of colloidal sulphur<sup>1)</sup>, but does not seem to be a specific property of that colloid.

The frequently recorded dependence of the value limit on the previous history becomes more comprehensible by these experiences. Further researches concerning all the above cited questions, as to the density of the sols (on which we already carried out a few series of measurements) and other correlated problems must be postponed till more peaceful times.

Utrecht.

VAN 'T HOFF-Laboratory.

**Chemistry.** — “*Action of sodium hypochlorite on amides of  $\alpha$ -oxyacids. A new method for the degradation of sugars.* By R. A. WEERMAN. (Communicated by Prof. FRANCHIMONT).

(Communicated in the meeting of February 27, 1915).

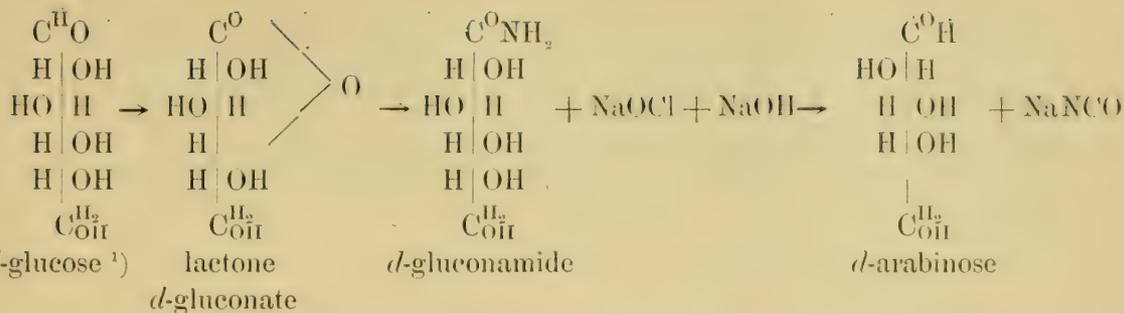
In a previous communication<sup>2)</sup> a method was described by me for the degradation of amides of  $\alpha$ - $\beta$  unsaturated acids to the aldehydes containing one atom of carbon less.

It now seemed possible to degrade in the same manner the amides of  $\alpha$ -oxyacids. The experiment has confirmed this supposition.

<sup>1)</sup> SVEN ODEN, *Der kolloide Schwefel*, Upsala 1913.

<sup>2)</sup> Proc. 1909; more fully in *LIEBIG'S Annalen* **401**, 1 [1913].





The *d*-gluconamide is prepared by passing ammonia into the absolute-alcoholic solution of the lactone. It crystallises in needles m. p. 142°—143°  $[\alpha]_D^{12} = +33,8^\circ$ . The rotation in aqueous solution slowly retrogrades, probably due to saponification. In an impure condition the amide has already been prepared by IRVINE, THOMSON and GARRETT. <sup>2)</sup>

The *d*-arabinose obtained from the amide with alkaline hypochlorite solution was isolated as diphenylhydrazone <sup>3)</sup>. It melted at 202°—203° (corr. 206°—207°). TOLLENS and MAURENBRECHER <sup>4)</sup> give as the melting point 204°—205°.

0,1348 gr. gave 10,4 c.c.N at 14° C and 755 mm.

Found: 8,97 % N

Calculated for  $\text{C}_{17}\text{H}_{20}\text{O}_4\text{N}_2$ : 8,86 % N

The melting point of a specimen of diphenylhydrazone, prepared from *d*-arabinose, which I received from the laboratory of the Department of Finances at Amsterdam through the agency of Prof. BLANKSMA, and which had been prepared according to RUFF's method, was likewise found to melt at 202°—203°; a mixture of the two melted at the same temperature.

The yield of hydrazone amounted to 50 % of the theoretical amount calculated on amide.

From the diphenylhydrazone the *d*-arabinose was liberated with formaldehyde. M.p. 156°—157°  $[\alpha]_D^{10} = -105,7^\circ$  (24 hours after dissolving.)

0,1018 gram gave 0,1488 gram  $\text{CO}_2$  and 0,0633 gram  $\text{H}_2\text{O}$ .

Found: 39,86 % C; 6,90 % H

Calculated for  $\text{C}_5\text{H}_{10}\text{O}_5$ : 40 % C; 6,67 % H

<sup>1)</sup> For the sake of convenience the aldehyde formula is used here for the sugars.

<sup>2)</sup> J. Ch. Soc. **103**, 245 [1913].

<sup>3)</sup> NEUBERG, Zeitschr. f. physiologische Ch. **35**, 34 [1902].

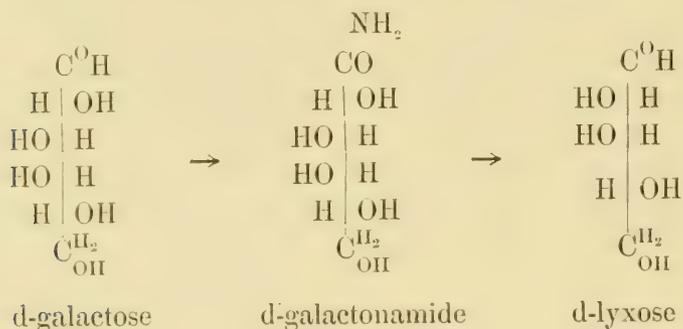
<sup>4)</sup> Ber. **38**, 500 [1905]. NEUBERG's statement as to the melting point being 218° is incorrect (see TOLLENS).

The fact that in the oxidation of *d*-gluconamide with sodium hypochlorite sodium isocyanate is also formed was demonstrated by addition of hydrazine sulphate, neutralisation and subsequent addition of benzaldehyde.

The precipitate formed contained beside benzalazine, benzalsemicarbazone, which were separated by means of ether.

*Degradation of d-galactose.*

*d*-galactose was degraded in exactly the same way to *d*-lyxose.



The *d*-lyxose was isolated as parabromophenylhydrazone.<sup>1)</sup> Melting point 156°—157°.

0,1488 gram gave 11,3 c.c. N at 16° C. and 762 m.m.

Found: 8,83 % N.

Calculated for C<sub>11</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub> Br.: 8,78 % N.

On mixing it with a specimen of *p*-bromophenylhydrazone from *d*-lyxose, prepared according to RUFF's method, and which I likewise received from the laboratory at Amsterdam, the melting point remained unchanged.

I want to point out that the preparation of the amides of the pentonic and the hexonic acids is easy of execution, as the lactones need not be isolated in a crystallised condition. For instance, from the calcium salt of *d*-galactonic acid I obtained a yield of 95 % of *d*-galactonamide. Mannonamide and arabanamide are also readily formed in this manner. With gluconamide the yield is less favourable because the formation of the lactone does not take place normally<sup>2)</sup>.

<sup>1)</sup> ALBERDA VAN EKENSTEIN and BLANKSMA, Chem. Weekbl. **11**, 191 [1914]. LEVENE and LA FORGE, Journ. of Biol. Ch. **18**, 325 [1914].

<sup>2)</sup> NEF, LIEBIG'S Annalen **403**, 322 [1914].

I am occupied with the application of the above described degradation method to other sugars such as pentoses.

The more fully detailed communication will be given elsewhere.

I have to tender my thanks to Prof. BLANKSMA for kindly giving me the opportunity to work in the organic-chemical laboratory of the University.

Leiden, February 1915.

Organic-Chemical  
Laboratory of the University.

**Physics.** — “*Theoretical determination of the entropy constant of gases and liquids.*” By H. TETRODE. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of Febr. 27, 1915).

§ 1. *Introduction and survey.*

If the entropy of an ideal gas per gramme molecule for the temperature  $T$  and the pressure  $p$  is given by:

$$S = C_p \log T - R \log p + a + C_p, \quad \dots \quad (1)$$

in which  $R$  is the gas constant and  $C_p$  denotes the heat capacity under constant pressure assumed as invariable for the range of temperature considered, then  $a$  is a constant remaining undetermined in classical thermodynamics. This value has, however, a definite value according to NERNST's heat theorem, when namely the entropy is defined so that it becomes zero for  $T = 0$  for the condensed gas, i. e. for a chemically homogeneous solid or liquid substance, which we shall always tacitly supposed to be done in what follows. Then we can determine  $a$  from measurements of the vapour tension, when we also know the course of the specific heat of the solid (or liquid) substance also at the lowest temperatures<sup>1)</sup>.

On the ground of a general definition of the thermodynamic probability in connection with the hypothesis of quanta I have derived the value of  $a$  for different cases in a previous paper<sup>2)</sup>, in which, however, at first undetermined universal values  $z$ ,  $z_1$ , and  $z_2$  still occurred, which I supposed to be  $= 1$ , while others thought they had to assign a different value at least to  $z^3$ ).

1) The quantity  $C = \frac{a}{R} \log_{10} e$  is generally called the chemical constant of the gas.

2) H. TETRODE, Ann. d. Phys. **38**, 434 and **39**, 255 (1912).

3) O. SACKUR, Ann. d. Phys. **40**, 67 (1913).

In what follows we shall now determine the entropy constant  $a$  through the direct calculation of the vapour tension according to classical statistical mechanics, hence for higher temperatures, while we shall of course have to know again the thermodynamic behaviour of the condensed phase for very low temperatures; the latter is, however, the case at present for solid substances on certain simplifying suppositions. In this way we shall not only get a direct confirmation of the formulae given before (with  $z = z_1 = z_2 = 1$ ), but shall also be able to establish the general<sup>1)</sup> definition of probability (of course for higher temperatures) for gases and liquids, which must be applied for the entropy determination.

As a further elucidation of the results found for multi-atomic molecules we shall also insert a few hypothetical considerations on the forces acting in the chemical binding between the atoms.

The main point in our considerations is the discussion of the exchangeability of similar atoms and molecules and of the influence of this on the thermodynamic probability and the entropy.

## § 2. *Suppositions on the properties of the solid substance.*

As we shall have to know the entropy of the solid substance, and as we can only give this at present theoretically when the motions of the molecules and atoms consist of sine vibrations, hence when the potential energy is a quadratic function of their coordinates, we shall have to suppose this of our solid substance. We may do this when the amplitude of the molecular motion is slight on the whole, when the molecules therefore depart little from their position of equilibrium. This, however, does not exclude that some rare molecules possessing an exceptionally great energy pass over larger distances, for which the general assumption does not hold, that they even now and then slip through between the surrounding molecules, or can detach themselves from the molecule complex, and pass into the vapour state, provided their number be so small at the considered temperature that it may be neglected for the calculation of averages.

Our assumption implies that the volume of the solid substance is independent of pressure<sup>2)</sup> and temperature. The specific heat at constant pressure then becomes equal to that at constant volume, whereas in reality it is as much as from  $\frac{1}{4}$  to 12 % greater at the temperatures that are to be considered. Though our theoretical

<sup>1)</sup> Cf. however, the conclusion of § 3.

<sup>2)</sup> Large pressures do not occur in our problem.

substance in this respect differs more or less from a real substance, yet this will not cause a very great error in the final result, seeing that the difference is comparatively small. It seems even probable to me that when we consider a system approaching reality still more closely whose vibrations are not purely sine shaped, an accurate knowledge of the thermodynamic behaviour of it at low temperatures would lead us to no other final result for the entropy constant of the gas, that therefore the expressions to be found possess universal validity.

The thermal energy of a solid substance as assumed by us according to a formula which has been accepted and confirmed of late years, is given by :

$$U = \sum \frac{h\nu_i}{e^{\frac{h\nu_i}{kT}} - 1} + \text{const.},$$

in which  $h$  and  $k$  are the constants of PLANCK, while the summation is to be extended over all the degrees of freedom of the system, each of a frequency  $\nu_i$ . The entropy is then given by :

$$S = \int \frac{1}{T} \frac{dU}{dT} dT = \sum \frac{h\nu_i}{T} \cdot \frac{1}{e^{\frac{h\nu_i}{kT}} - 1} - k \sum \log \left( 1 - e^{-\frac{h\nu_i}{kT}} \right), \quad (2)$$

which for the higher temperatures, with which we shall be exclusively occupied in what follows, passes into :

$$S = k \sum \left( 1 - \log \frac{h\nu_i}{kT} \right) = k\lambda \left( 1 - \overline{\log \frac{h\nu}{kT}} \right), \quad \dots \quad (3)$$

in which  $\lambda$  is the number of degrees of freedom, and the line expresses the mean value.

### § 3. Calculation of the vapour pressure of a monatomic solid substance and of the entropy constant of the gas<sup>1)</sup>.

Let us now consider a gramme molecule of a monatomic substance consisting of  $N$  molecules, inclosed within the invariable volume  $V$  and in temperature equilibrium with its surroundings. This system may then be considered as part of a much larger one of the same temperature. If  $q_1, \dots, q_{3N}$  are the coordinates of the molecules,

<sup>1)</sup> A similar calculation with the correct final result has already been published by O. STERN (Phys. Zeitschr. **14**, 629 (1913)), however with an imaginary solid substance, which perhaps departs somewhat too much from reality. Nor is in this way the occurrence of  $N!$  in the general formula (see below), caused by the exchangeability of the molecules, made clear.

$p_1, \dots, p_{3N}$  the corresponding quantities of motion, then the probability that at an arbitrarily chosen moment the system will be in a state for which the coordinates will successively have values lying between  $q_1$  and  $q_1 + dq_1$ ,  $q_2$  and  $q_2 + dq_2$  etc., and the quantities of motion between  $p_1$  and  $p_1 + dp_1$ , etc., will be given by :

$$w dG = w(p_1, \dots, q_{3N}) dp_1 \dots dq_{3N} = I e^{-\frac{E}{kT}} dp_1 \dots dq_{3N}, \dots \quad (4)$$

in which  $E$  is the energy of the system, and

$$\frac{1}{I} = \int \dots \int e^{-\frac{E}{kT}} dp_1 \dots dq_{3N}$$

the integration being extended over all the values of the  $q$ 's within the volume  $V$  and all the  $p$ 's from  $-\infty$  to  $+\infty$ .<sup>1)</sup>

If we now assume that  $T$  and  $V$  have been chosen so that part of the system is gaseous, the other solid, we may write for the probability that the molecules 1 up to  $n$  ( $n$  inclusive) are in the gaseous state,  $n+1$  up to  $N$  ( $N$  inclusive) on the other hand in the solid state, as follows :

$$\left( \int w dG \right)_n = I \int e^{-\frac{\varepsilon}{kT}} dp_1 \dots dq_{3n} \int e^{-\frac{\varepsilon'}{kT}} dp_{n+1} \dots dq_{3N}, \dots \quad (5)$$

in which the  $6n$ -fold integral must be taken with respect to the gaseous part of the system, the  $6(N-n)$ -fold one with respect to the solid part. The volumes of both are determined by  $V$  and the volume of the solid part that is only dependent on  $N-n$ .<sup>2)</sup> Further :

$$\varepsilon = \frac{1}{2m} (p_1^2 + \dots + p_{3n}^2)$$

is the energy of the gas,

$$\begin{aligned} \varepsilon' = \varepsilon'_p + \varepsilon'_q + n'c = & \frac{1}{2m} (p_{3n+1}^2 + \dots + p_{3N}^2) + \\ & + \sum_{3n+1}^{3N} \sum_{3n+1}^{3N} a_{ij} q_i q_j + \sum_{3n+1}^{3N} b_i q_i + b_0 + n'c, \end{aligned}$$

in which  $N-n = n'$  is put, the energy of the solid body, so  $\varepsilon + \varepsilon' = E$ .  $c$  and the  $a$ 's and  $b$ 's are constants;  $-c$  is the work which is to be applied to detach a molecule resting in its position

<sup>1)</sup> We may also say that the system, as it is at a definite moment, forms part of a canonical ensemble, with modulus  $kT$ .

<sup>2)</sup> In principle also other arrangements of the molecules than those of solid substance or gas are of course conceivable, at least for a short time; they will, however, be so improbable, that they may be disregarded. Nor is it necessary to consider a solid phase of variable density.

of equilibrium from its connection with the solid body, and to bring it in the gas space, hence  $c$  is negative.

We can immediately integrate with respect to the gas, through which we get:

$$\left( \int w dG \right)_n = I (2\pi m kT)^{\frac{3n}{2}} v^n \int e^{-\frac{\varepsilon'}{kT}} dp_{3n+1} \dots dq_{3N}, \dots \quad (6)$$

in which  $v$  is the volume of the gas.

Now we can replace the values  $q_{3n+1}$  to  $q_{3N}$  (inclusive) by variables  $q'_1, \dots, q'_{3n'}$  which are in linear connection with them,

so that  $\varepsilon'_q = \frac{1}{2} \sum_1^{3n'} f_i q_i'^2$  with all positive  $f$ 's, while  $\varepsilon'_p = \frac{1}{2m} \sum_1^{3n'} p_i'^2$ ,

when  $p'_i$  is the value corresponding to  $q'_i$ , hence  $\frac{\partial \varepsilon'}{\partial q'_i}$ . The quantities

$q'_i$  are evidently a criterion for the deviations of the molecules from their positions of equilibrium.

As according to a known thesis  $dp_1' \dots dq'_{3n'} = dp_{3n+1} \dots dq_{3N}$ , we get:

$$e^{-\frac{\varepsilon'}{kT}} dp_{3n+1} \dots dq_{3N} = e^{-\frac{n'c}{kT}}, e^{-\frac{\sum \frac{1}{2} f_i q_i'^2 + \sum \frac{1}{2m} p_i'^2}{kT}} dp_1' \dots dq'_{3n'} \quad (7)$$

When we however should simply integrate on the right with respect to all the values of  $-\infty$  to  $+\infty$ , and substitute the result in (6), as being equal to the integral with respect to the leftside member of (7), we should commit a serious error and arrive at an absurd final result.

We had namely originally to integrate with respect to all the values of the  $q$ 's inside the volume occupied by the solid body. In this those values are naturally left out of account for which the energy is very great, for which a molecule is therefore pretty far from its position of equilibrium, as this according to the formula for the probability very rarely occurs. The proportionality of the energy with  $q'^2$ , however, only holds for slight departures out of the position of equilibrium, and no longer when a molecule has got so far that it can pass between the neighbouring ones. This must actually occasionally occur, though very seldom, and in this way two molecules can interchange their original positions, and each molecule can successively be found at all possible points of the solid body, and have a position of equilibrium which was before

peculiar to another.<sup>1)</sup> This new position is a priori as probable as the preceding one.

As it is now tacitly assumed by simply integrating the righthand side of (7) over the range from  $-\infty$  to  $+\infty$  that a molecule cannot leave its place, the thus obtained integral must still be multiplied by  $n!$ , this being the number of the interchanges possible between the molecules of the solid body.

When this is taken into account, we find:

$$\left( \int v dG \right)_n = I e^{-\frac{nc}{kT}} (2\pi m kT)^{3/2n} v^n n! (kT)^{3n'} \Pi, \quad \dots \quad (8)$$

in which  $\Pi$  denotes the product of the  $3n'$  values  $\left( \frac{4\pi^2 m}{f_i} \right)^{1/2}$ .

This is therefore the probability that the molecules from 1 to  $n$  inclusive form a gas with the volume  $v$ , the  $n'$  remaining ones a solid body with the volume  $v' = V - v$ .<sup>2)</sup>

It is, however, of no importance whatever for thermodynamics whether it is just the molecules numbered 1 up to  $n$  that are in the gas state. What we want to know is rather the probability that  $n$  arbitrary molecules are in the gas state, the remaining ones in the solid state. This probability, which we shall call  $W(n)$ , is obtained by multiplying the expression (8) by  $\frac{N!}{n!n'!}$ , being the number of different ways in which the  $N$  molecules can be divided between gas and solid body on the condition that always  $n$  remain in the gas.

We get:

$$W(n) = I \frac{N!}{n!} e^{-\frac{nc}{kT}} (2\pi m kT)^{3/2n} v^n (kT)^{3n'} \Pi \quad \dots \quad (9)$$

Bearing in mind that  $\frac{1}{2\pi} \sqrt{\frac{f_i}{m}}$  is the frequency  $\nu_i$  for the variable  $q_i'$ , we may also write:

$$\log W(n) = \log I + N \log N - N - n \log n + n - \frac{nc}{kT} + \frac{3}{2} n \log (2\pi m) + \left. \begin{aligned} &+ \frac{3}{2} n \log (kT) + n \log v - 3n' \overline{\log v} + 3n' \log (kT), \end{aligned} \right\} \quad (10)$$

in which  $\overline{\log v}$  is the mean value of  $\log v_i$ .

<sup>1)</sup> In this it is assumed that the energy required for a molecule to slip through the surrounding ones, is not infinite; at any rate it is, however, possible to imagine the interchange of the molecules to be brought about by evaporation and renewed condensation, which must really continually take place at the surface.

<sup>2)</sup> As we have assumed the density of the solid substance to be invariable,  $v' = V - v$  is determined by  $n'$ , and therefore by  $n$ .

In order to find the most probable distribution of the molecules between gas and solid substance for given values of  $T$  and  $V$ , which is the only one that need be considered for the thermodynamical equilibrium, we must see for what value of  $n$  the function  $W(n)$  is a maximum, so that  $\delta W = 0$ , or what comes to the same thing  $\delta \log W = 0$ .

As  $\delta n' = -\delta n$ ,  $\frac{\delta v}{v} = -\frac{v'}{v} \cdot \frac{\delta v'}{v'} = 1) -\frac{v'}{v} \cdot \frac{\delta n'}{n'} = +\frac{v'}{v} \cdot \frac{\delta n}{n}$ , and  $I$  is independent of  $n$ , we get the equation:

$$0 = -\log n + \frac{c}{kT} + \frac{3}{2} \log(2\pi m) + \log v + \frac{nv'}{n'v} + 3 \overline{\log v} - \frac{3}{2} \log(kT) \quad (11)$$

We know from the ordinary kinetic gas theory that the pressure  $p$  of the gas is  $\frac{nkT}{v}$ , on account of which we may write for (11):

$$0 = \frac{c}{kT} + \frac{3}{2} \log(2\pi m) - \log p + \frac{pv'}{n'kT} + 3 \overline{\log v} - \frac{1}{2} \log(kT) \quad (12)$$

The entropy  $S'$  of a gramme molecule of solid substance is now (see § 2)  $= 3kN \left(1 - \log \frac{hv}{kT}\right)$ .

Equation (12) then becomes:

$$0 = \frac{c}{kT} + \frac{3}{2} \log(2\pi m) - \log p + \frac{pv'}{n'kT} - \frac{S'}{kN} + \frac{5}{2} \log(kT) - 3 \log h + 3 \quad (13)$$

It is further clear that the increase of the internal energy at the evaporation amounts to 2):

$$U = -Nc + \frac{3}{2} kNT - 3kNT = -Nc - \frac{3}{2} kNT. \quad (14)$$

If  $S$  is now the entropy of a gramme molecule of gas, the increase of entropy at the evaporation is:

$$S - S' = \frac{U + \left(\frac{N}{n}v - \frac{N}{n'}v'\right)}{T} = -\frac{Nc}{T} - \frac{1}{2} kN - \frac{Npv'}{n'T} \quad (15)$$

We finally find for  $S'$  from (13) and (15):

$$S = kN \left\{ \frac{5}{2} \log(kT) - \log p + \frac{3}{2} \log(2\pi m) - 3 \log h + \frac{5}{2} \right\} \quad (16)$$

KÖHNER and WINTERNITZ<sup>3)</sup> have calculated the chemical constant of hydrogen for low temperatures, in which this behaves as a mona-

1) On account of the constant density  $\frac{v'}{n}$ .

2) A possible zero point energy had to be simply taken into account in  $c$  here and in the following §§.

3) v. KÖHNER und P. WINTERNITZ, Phys. Z.S. 15, 393 and 645 (1914).

tomic gas <sup>1)</sup>, from thermochemical data; they have found with the atmosphere as pressure unity:

$$C = -1,303$$

with an uncertainty which they estimate at most at  $\pm 0,15$ . They calculate from (16):

$$C = -1,17,$$

which may be considered as a very satisfactory agreement.

On the other hand O. STERN <sup>2)</sup> has also derived the entropy of monatomic gaseous iodine from thermochemical data, and found a value which very greatly deviates from that following from (16). He infers from this that either the heat theorem is not valid for the reaction  $2I_{solid} \rightleftharpoons I_{2solid}$ , that therefore the difference of entropy remains finite for  $T=0$ , or that the vapour tension of monatomic iodine cannot be accurately calculated with the aid of (16). He seems to think the former rather probable. It seems to me that they come to the same thing. It may namely be very well the case that the heat theorem only holds for substances that really exist, and this cannot be said of monatomic solid iodine. Then the calculation of the vapour tension as we have carried it out in this §, has no longer any meaning: monatomic gaseous iodine cannot exist at low temperatures either. The formulae of this and the following §§ for the entropy constant can lay claim to validity only for such substances as also occur in the same molecular form at low temperatures, as the gases of the He group, the metal vapours, further also gases as  $H_2$ ,  $O_2$ ,  $CO$ ,  $I_2$  etc.; but not gases as  $I$ ,  $Br$  or such like ones. Of course the possibility continues to exist that an unexpectedly great error occurs in the data used by STERN.

§ 4. *On the vapour pressure of a diatomic solid substance and the entropy constant of the gas.*

In a corresponding way the vapour pressure of a diatomic substance and the entropy of the vapour can be calculated, when it is assumed that here too the atom motions consist of sine vibrations, while moreover the two atoms of one molecule are always at a definite distance from each other <sup>3)</sup> as they also are in the gas for

<sup>1)</sup> A. EUCKEN, Sitz. Ber. Berl. Akad., 1 Febr. 1912.

<sup>2)</sup> O. STERN, Ann. d. Phys. **44**, 497 (1914).

<sup>3)</sup> When the possibility of existence of the solid substance falls below the region within which classical mechanics may still be applied to the rotation of the molecules, the calculation has of course no direct meaning, and it will be preferred to follow another method; see § 5.

A possible mutual vibration of the atoms with a zero point energy  $\frac{1}{2}h\nu$  would

an extensive temperature region, so that the molecule has five degrees of freedom. It is then still necessary to assume that at a definite point of the solid body which is to be thought as a crystal, the molecule axis passing through the centres of gravity of the atoms can only have one definite direction, from which it will of course deviate periodically by small angles on account of the heat motion. If the two atoms are then still supposed to be different, so that the opposite direction does not mean the same thing, and is therefore not possible, we find for the entropy of the gas<sup>1)</sup>:

$$S = kN \left\{ \frac{7}{2} \log(kT) - \log p + \frac{3}{2} \log(2\pi m) + \log(2\pi J) - 5 \log h + \log(4\pi) + \frac{7}{2} \right\}, \quad (17)$$

and for the constant  $a$

$$\frac{a}{R} = \frac{7}{2} \log k + \frac{3}{2} \log \frac{2\pi m}{h^2} + \log \frac{2\pi J}{h^2} + \log(4\pi), \quad \dots \quad (18)$$

in which  $J$  is the principal moment of inertia of a molecule, of course for an axis which is normal to that passing through the centres of gravity of the atoms.

If on the other hand we assume the two atoms in the molecule as perfectly equal and indistinguishable, so that at any point in the crystal the axis of the molecule might as well be rotated by  $180^\circ$ , we find for  $S$ , resp.  $a$  a  $kN \log 2$  smaller value. In the formula analogous with (8) we get then namely  $2^{n'} n'!$  instead of  $n'!$ .

In reality we shall have to assume at least in most cases, that also 2 similar atoms in a molecule perform a different function, e.g. that one is positive, the other electrically negative, or else that the molecule possesses a magnetic moment, that they are therefore indeed to be distinguished and the molecule can only have one direction at any place in the crystal. Then the formulae (17) and (18) will be universally valid.

### § 5. *On the dissociation of di-atomic gas molecules.*

We can come to the same conclusion when we investigate the dissociation of a di-atomic gas statistically-mechanically, and assume the formula (16) for the entropy of the mon-atomic components to be correct.

We must then assume that the atoms in the molecule vibrate against each other with a frequency  $\nu$ , so that the energy of the

render the distance variable by only a practically insignificant amount for molecules consisting of heavier atoms; for hydrogen this would, however, be considerable. (The value of  $\nu$  may be calculated from the specific heat at high temperatures, the moment of inertia from EUCKEN's experiments and formulae (16) and (17)).

<sup>1)</sup> For the calculation cf. §§ 6 and 7.

vibration becomes  $= \frac{h\nu}{e^{kT} - 1} + \text{const.}$  according to the formula of

PLANCK-EINSTEIN. It could be neglected for the temperatures that are to be taken into account for the evaporation<sup>1)</sup>. For very high values of the energy of vibration, which, however, will be so rare at not too high temperatures that they may be left out of account in the calculation of the mean value, the mutual motion of the atoms is no longer a simple sine vibration; and at still greater value of the energy the attractive force between the atoms becomes very small, they get detached from each other, and the molecule is dissociated.<sup>2)</sup>

We may imagine that each of the (spherical) atoms has a pole, and that in the molecule the two poles coincide or are removed from each other a small distance through the heat motion, however in such a way that the axes of the two atoms passing through pole and centre are always in the production of each other.

When the atoms are of different kinds, say A and B, we find for the constant of equilibrium of the reaction  $AB \rightleftharpoons A + B$ <sup>3)</sup>:

$$\frac{n_2}{n_1} = e^{-\frac{c}{kT}} \left( \frac{m_A m_B}{m_A + m_B} \right)^{3/2} \cdot \frac{1}{J} \cdot \frac{1 - e^{-\frac{h\nu}{kT}}}{h} \cdot \frac{1}{2} \sqrt{\frac{kT}{2\pi}}, \dots \quad (19)$$

in which  $n_2$  resp.  $n_1$  is the number of split resp. unsplit molecules per volume unity,  $m_A$  and  $m_B$  the masses of the atoms, and  $J$  the moment of inertia of the molecule.  $c$  is the heat of dissociation, as it would be for the absolute zero.

For lower temperatures this reduces to:

$$\frac{n_2}{n_1} = e^{-\frac{c}{kT}} \left( \frac{m_A m_B}{m_A + m_B} \right)^{3/2} \frac{1}{2Jh} (kT)^{3/2} \dots \dots \dots (20)$$

On the other hand according to thermodynamics:

$$\frac{n_2}{n_1} = A e^{-\frac{c}{kT}} T^C \left( \frac{1}{kT} \right)^{2-1}, \dots \dots \dots (21)$$

in which  $\log A = \frac{a_A + a_B + a_{AB}}{R}$ ,  $c$  has the same meaning as in (20)

<sup>1)</sup> If namely a possible zero point energy is not so great that the moment of inertia becomes variable in consequence.

<sup>2)</sup> In reality it may of course occur that the vibrations are already no longer sine-shaped for small values of the energy; it is, however, not possible for the present to take this into account theoretically.

<sup>3)</sup> J. D. VAN DER WAALS Jr., these Proceedings XVI, p. 1082.

and  $c$  is the algebraic sum of the heat capacities of the reacting gases at constant pressure, divided by  $R$ , i. e.  $= \frac{5}{2} + \frac{5}{2} - \frac{7}{2} = \frac{3}{2}$ .  $a_A$ ,  $a_B$  and  $a_{AB}$  are the entropy constants of the gases defined in (1).

By equating (20) and (21) we find :

$$\begin{aligned} \frac{3}{2} \log m_A + \frac{3}{2} \log m_B - \frac{3}{2} \log m_{AB} - \log(2J) - \log h + \frac{1}{2} \log(kT) - \frac{1}{2} \log(2\pi) = \\ = \frac{a_A}{R} + \frac{a_B}{R} - \frac{a_{AB}}{R} + \frac{1}{2} \log T - \log k, \end{aligned}$$

in which  $m_{AB} = m_A + m_B$  is the mass of a molecule  $AB$ .

When in this we substitute for  $a_A$  and  $a_B$  the values following from (16) and (1), we find :

$$\frac{a_{AB}}{R} = \log J + \frac{7}{2} \log k - 5 \log h + \frac{3}{2} \log m_{AB} + \frac{1}{2} \log 2 + \frac{7}{2} \log \pi,$$

corresponding to (18).

When, however, we assume the two atoms to be of the same kind, we shall find a value of half the amount for the dissociation constant  $\frac{n_2^2}{n_1}$  in the kinetic calculation : the probability that two atoms meet that can unite is now namely twice as great as before, all the rest remaining the same.

Thermodynamically we find, however, a four times smaller value : in (21)  $\frac{(2n_2)^2}{n_1}$  must then be substituted for  $\frac{n_2 \times n_2}{n_1}$ , the righthand side remaining unchanged. In this case, just as in the preceding §, we should, therefore, find an  $R \log 2$  smaller value for  $a_{AB}$ .

As, however, as was said above, it must be generally assumed that two similar atoms do not perform the same function in chemical combination, we shall have to give a somewhat more general form to the suppositions made by VAN DER WAALS Jr. about the chemical forces. We suppose every atom to possess two poles, a positive and a negative one, and that in a certain combination of two dissimilar atoms  $A$  and  $B$  always e.g. the positive pole of  $A$  gets in contact with the negative pole of  $B$ . In a combination of two similar atoms the positive pole of the one will always be connected with the negative pole of the other ; in this case it is of no consequence, however, which atom is connected through its positive, which through its negative pole. This makes the number of possibilities of binding still  $2 \times$  greater than for dissimilar atoms, and the change of coming together becoming already  $2 \times$  greater through the mere fact of the atoms being equal (see above), it now becomes  $4 \times$  greater, which is in harmony with the thermodynamic formula, so that also in this case we have to assign the value (18) to  $a_{AB}$ .

It should, however, be kept in view that the suppositions on the chemical forces used in this §, possibly do not sufficiently agree with reality; nor do they any longer appertain to pure classical mechanics: we have, namely, assumed that in case of a chemical binding the atoms must have a definite relative orientation, though we have not spoken at all of a rotation of the atoms. We might imagine other representations of the acting forces, but the one used seems to me the simplest and the most obvious. After what has been said at the conclusion of § 3, it will be clear that the application of (16) is probably not permissible for the entropy of the monatomic components, viz. in the case of one kind of atoms.

The contents of this § is then only interesting from a theoretical point of view, viz. to show how the same result as in § 4 can be found in another way too. A third derivation of the entropy constant of the rotation for di-atomic molecules has been given by O. STERN<sup>1)</sup> by the aid of LANGEVIN'S theory of paramagnetism. From this we see that this derivation only holds for the case that the two atoms do not perform the same function. The result agrees with ours.

§ 6. *General formula for the vapour pressure of a multi-atomic solid substance and the entropy of the vapour.*

We will now calculate the vapour pressure of arbitrary multi-atomic solid substances in an analogous way as we did in § 3 for monatomic ones. We then only assume (for simplicity's sake)<sup>2)</sup> that the vapour is an ideal gas, i.e. a gas with independent molecules, whose energy, therefore, does not depend on the volume; the specific heat, however, may indeed vary with the temperature, if only classical mechanics remain of application. Hence the internal molecule movements need not exclusively consist of rotations and sine vibrations. For the solid substance we continue, of course, to consider the suppositions of § 2 as valid, to which we may add, as in § 4 that at every place in the crystal the molecule present there can only have one definite orientation.<sup>3)</sup>

Thus we find for the probability that  $n$  of the  $N$ -molecules belong to the vapour, the formula which is analogous with (10):

<sup>1)</sup> O. STERN, Ann. d. Phys. **44**, 497 (1914).

<sup>2)</sup> It is shown in § 8 that the formula to be found for the entropy holds just as well for non-ideal gases and for liquids.

<sup>3)</sup> The impossibility of another orientation must of course be understood so that a very great energy would be required for this.

$$\log W(n) = \log I + \log \Phi - \frac{n'c}{kT} + N \log N - N \left( \begin{array}{l} \dots \\ - n \log n + n + jn' \log(kT) - jn' \overline{\log r}, \end{array} \right) \quad (22)$$

in which  $j$  is the number of degrees of freedom per molecule,

$$\Phi = \int \dots \int e^{-\frac{\varepsilon}{kT}} dp_1 \dots dq_{jn}$$

and the other quantities have a meaning corresponding to that which they had before.  $\varepsilon$  is now of course the whole energy of the  $n$  gas molecules,  $\frac{1}{I}$  the  $jN$ -fold integral

$$\int \dots \int e^{-\frac{E}{kT}} dp_1 \dots dq_{jN}$$

As  $3n$  of the  $jn$  coordinates of the gas molecules denote the positions of the molecular centres of gravity, they do not occur in  $\varepsilon$ ; in consequence of this and on account of what was said above  $\Phi$  is of the form:

$$\Phi = v^n [f(T)]^n \dots \dots \dots (23)$$

in which the function  $f$  is a  $(2j-3)$ -fold integral referring only to one molecule, which therefore besides on  $T$ , depends only on the mechanical constants of the molecules. It follows from this that:

$$\frac{\partial \Phi}{\partial v} = \frac{n}{v} \Phi, \quad \text{or} \quad \frac{\partial \log \Phi}{\partial \log v} = n \dots \dots \dots (24)$$

The equation for the most probable value of  $n$ , hence for the thermodynamic equilibrium becomes:

$$0 = \frac{d \log \Phi}{dn} + \frac{c}{kT} - \log n - j \log(kT) + j \overline{\log r} \dots \dots (25)$$

Now:

$$\frac{d \log \Phi}{dn} = \left( \frac{\partial \log \Phi}{\partial n} \right)_v + \left( \frac{\partial \log \Phi}{\partial v} \right)_n \frac{dv}{dn} = \frac{1}{n} \log \Phi + \frac{n}{v} \cdot \frac{v'}{n'} \cdot \left( \frac{dv}{dn} = \frac{v'}{n'} \right)$$

just as in § 3).

Hence we get:

$$0 = \frac{1}{n} \log \Phi + \frac{n}{v} \cdot \frac{v'}{n'} + \frac{c}{kT} - \log n + j \log \frac{r}{kT} \dots \dots (26)$$

The entropy of the solid substance is:

$$S = k j N \left( 1 - \log \frac{hr}{kT} \right) \dots \dots \dots (27)$$

Further:

$$S - S' = -\frac{Ne}{T} + \frac{E}{T} - kjN \log \frac{p \left( \frac{N}{n} v - \frac{N}{n'} v' \right)}{T} \quad (28)$$

when  $E$  is the energy of  $N$  molecules of gas

$$\frac{N}{n} \cdot \frac{1}{\Phi} \int \dots \int \epsilon e^{-\frac{\epsilon}{kT}} dp_1 \dots dq_{jn} \dots \quad (29)$$

When it is borne in mind that  $pv = knT$ , it follows from (26), (27), (28), that:

$$S = -kN \log n + \frac{kN}{n} \log \Phi - kjN \log h + \frac{E}{T} + kN,$$

or when for the sake of simplicity we put  $n = N$ :

$$S = k \log \Phi - kN \log N + kN + \frac{E}{T} - kjN \log h. \quad (30)$$

Hence the free energy is:

$$F = E - TS = -kT \log \frac{\Phi}{h^j N N!} \dots \quad (31)$$

We find for the free energy, either by substituting the value (29) for  $E$  in (30), or by differentiating (31) with respect to  $T$ :

$$S = -k \int f \log f dG - k \log (h^j N) - k \log (N!), \dots \quad (32)$$

in which:

$$\frac{1}{\Phi} e^{-\frac{\epsilon}{kT}} = f \quad \text{en} \quad dp_1 \dots dq_{jn} = dG$$

§ 7. *Calculation of the entropy of gases with arbitrary rigid molecules.*

We will now apply the formulae (31), resp. (32) found in the preceding § to two simple cases of general occurrence.

We can of course first find back the formula (16) of § 3. We further find for a gas, the molecules of which possess two rotation degrees of freedom with the moment of inertia  $J$ , and will be rigid for the rest:

$$S = k \left\{ \frac{3}{2} N \log \frac{2\pi mkT}{h^2} + \log \frac{v}{N!} + N \log \frac{2\pi JkT}{h^2} + N \log (4\pi) + \frac{5}{2} N \right\} \quad (33)$$

which formula we already meet in §§ 4 and 5.

For rigid molecules with three rotation degrees of freedom and the chief moments of inertia  $J_1$ ,  $J_2$ , and  $J_3$ , we find:

$$S = k \left\{ \frac{3}{2} N \log \frac{2\pi mkT}{h^2} + \log \frac{v}{N!} + \frac{1}{2} N \log \frac{2\pi J_1 kT}{h^2} + \right. \\ \left. + \frac{1}{2} N \log \frac{2\pi J_2 kT}{h^2} + \frac{1}{2} N \log \frac{2\pi J_3 kT}{h^2} + N \log (8\pi^2) + 3 N \right\}. \quad (34)$$

Without entering further into the calculation it is yet easy to see the analogy of the formulae (33), (34), and (16). If we write the last in the form:

$$S = k \left\{ \frac{3}{2} N \log \frac{2\pi mkT}{h^2} + \log \frac{v}{N!} + \frac{3}{2} N \right\},$$

we see that in each of the three expressions per degree of freedom first of all a term  $\frac{1}{2} N \log \frac{2\pi mkT}{h^2}$  resp.  $\frac{1}{2} N \log \frac{2\pi JkT}{h^2}$  occurs, according as it is one of rectilinear or of rotatory motion. For the three degrees of freedom of rectilinear motion moreover a term  $\log \frac{v}{N!}$  is everywhere found. In this  $v$  is the three-dimensional extension of the coordinates denoting the place of the centre of gravity of a molecule, while the division by  $N!$  is caused by the interchangeability of the molecules, as has been fully set forth in § 3.

We find in (33)  $4\pi$  instead of  $v$  and in (34)  $8\pi^2$  for the rotatory motion. In (33)  $4\pi$  is the two-dimensional extension of the angular coordinates, which indicate the direction of that axis of the molecule round which it does not revolve, while in (34) another factor  $2\pi$  is added, being the extension of the third angular coordinate, which denotes the revolution round the said axis, which now, indeed, does take place. Finally there is everywhere still a term  $\frac{1}{2} N$  per degree of freedom.

§ 8. *On the general definition of the thermodynamic probability for gases and liquids.*

We know from ordinary statistical mechanics that the changes of the expressions (32) and (31) denote generally the change of the entropy, resp. free energy for changed values of  $v$  and  $T$ . As they, as we have seen, indicate for a system in one definite condition (ideal gas), the absolute values of  $S$  and  $F$ , (i.e. those with the accurate additive constant), they will have to do this for all conditions. In this it should of course be taken into account that  $\epsilon$  for smaller values of  $v$  can also depend on the mutual distances (and possibly orientations) of the molecules.

The formulae (31) and (32) are therefore of general validity on the suppositions made, also for non-ideal gases and for liquids,

which latter can namely be formed from gases in a continuous way. They would also have to hold for solid substances, when these were considered in the same way; as it is however customary to consider the molecules in this case as not interchangeable,  $N!$  resp. the term with  $\log(N!)$  must be omitted. This is namely the case when the solid substance is imagined as a system of fixed "oscillators".

Though properly speaking we have only generally proved the formulae on the assumption that the system can pass into an ideal solid body without loss of degrees of freedom, it yet seems plausible that a general validity may be ascribed to it.

We have, namely, seen in § 5 that it may also be derived in another way for a definite case, and the conclusion suggests itself that this will also be possible in other cases. We have, however, at the same time learnt to know the probable limits of the validity.

If we want to drop the supposition that no indistinguishable atoms occur in a molecule, we shall have to add still a term  $-kN \log p$  to (32), when  $p$  is the number of different ways, in which a molecule can be made to cover itself.

We can finally give still another form to (32). When the integration is replaced by a summation, and when in this  $dG = h^j N$  is always put, we get:

$$S = -k \sum f_i dG_i \log(f_i dG_i) - k \log(N!) - k \log(p^N). \quad (35)$$

When a canonical ensemble consists of so great a number  $M$  of systems that the number  $M_i = M f_i dG_i$  lying in an elementary region  $dG_i$  is a large number, we can write:

$$MS = -k \sum M f_i dG_i \log(M f_i dG_i) + kM \log M - kM \log(N!) - kM \log(p^N) = \\ k \log \frac{M!}{p^{MN} (N!)^M \cdot M_1! M_2! M_3! \dots} \quad \dots \quad (36)$$

This being the entropy of a system of  $MN$  molecules, the expression must only depend on the product  $MN$ , independent of the way in which this has been separated into factors. This may be seen still better as follows.

When in (35)  $N$  is replaced by  $MN$ , we get according to (23):

$$\Phi_{MN} = v \frac{MN}{MN} [f(T)]^{MN} = (Mv_N)^{MN} [f(T)]^{MN} = M^{MN} \Phi^{MN}.$$

Hence

$$f_{iMN} = \left( \frac{e^{-\frac{\epsilon_i}{kT}}}{\Phi} \right)_{MN} = \frac{f_{iN}^M}{M^{MN}},$$

because when corresponding elementary regions are compared,  $\epsilon_{MN} = N \cdot$

Further  $dG_{iMN} = h^j MN = (dG_{iN})^M$ .

Then  $\sum f_i dG_i$  taken over an arbitrary group of elementary regions, is the probability that the system lies in one of them; when this group is now chosen so that the interval  $\varepsilon_{MN}$  corresponding to it becomes equal to the  $M$ -fold of that of the group of a system of  $N$  molecules compared with the group, evidently:

$$(\sum f_i dG_i)_{MN} = (\sum f_i dG_i)_N$$

As the interval  $\Delta\varepsilon$  of  $\varepsilon$  may be chosen so small that  $\frac{\Delta\varepsilon}{kT} = 0$  may be put, the argument of the logarithm in (35) may be put constant in the summation extended over a group.

In this way we get:

$$\begin{aligned} S_{MN} = & -k \sum f_{i,MN} dG_{i,MN} \log (f_{i,MN} dG_{i,MN}) - k \log (MN)! - k \log (p^{MN}) = \\ & -k \sum f_i dG_i \log \left( \frac{f_{iN}^M}{M^{MN}} [dG_{iN}]^M \right) \\ & - kMN \log M - kMN \log N + kMN - kMN \log p = -kM \sum f_i dG_i \log (f_i dG_i) \\ & + k(MN \log M) \cdot (\sum f_i dG_i) + \text{etc.} = \end{aligned}$$

(as  $\sum f_i dG_i = 1$ )

$-kM \sum f_i dG_i \log (f_i dG_i) - kMN \log N + kMN - kMN \log p = MS_N$ , which we have now derived from an expression depending only on the product  $MN$ , which expression we had, of course, to treat differently, as far as  $M$  and  $N$  are concerned.

Prof. LORENTZ, whose communication "*Opmerkingen over de theorie der eenatomige gassen*"<sup>1)</sup> induced me to take up the treated problems, points out to me, among different valuable remarks, for which I am greatly indebted to him, that I have now indeed demonstrated that my formulae may be considered as convenient precepts for the calculations for the thermodynamic probability of the gas, but that I have not yet explained how through the consideration of the gas alone they could be derived, in particular why after all it is in this case necessary to divide by  $N!$ . This is a difficult question. In some connection with it is what follows:

We have seen that a di-atomic gas, the molecules of which consist of perfectly equal atoms, at higher temperatures must have a  $k \log (2^N)$  smaller entropy than when the atoms are different. Must not the specific heat of the gas then have a different course in the two cases at low temperatures, and how could this be accounted for?

<sup>1)</sup> H. A. LORENTZ, Zittingsversl. Akad. Amsterdam, **23**, 515 (1914). Not yet translated.

Or will the entropy of the gas, which is monatomic from a thermodynamic point of view at very low temperatures, perhaps not be represented by (16), but have a value  $kN \log 2$  smaller? This seems improbable, at least at first sight. A perfectly satisfactory answer to this question is probably to be expected only from a general theory of quanta.

However, something can be said about the division by  $N!$  also without having recourse to the solid phase. Suppose we have the general theory of quanta. We come to the conclusion that for the determination of the thermodynamic probability we have not to reckon with infinitely small regions, but with such of a definite finite extent. This, however, holds only without reservation for systems the molecules of which are all different. Of a gas for which this is the case, we could not say that the entropy was proportional to the mass; it would much sooner contain a term  $k \log N!$ . Now, however, the entropy of a mixture of different gases is  $k \log \frac{N!}{n_1! n_2! \dots}$  greater than when the gases are equal, which can be thermodynamically derived for large values  $n_i$  etc., while it seems natural to consider it also as valid for small  $n_i$ 's, ( $n_i$  etc. are of course the numbers of molecules for the different kinds,  $N$  is  $= \sum n_i$ ). If now all  $n_i$ 's are  $= 1$ , in other words, if the gas consists of nothing but different molecules, the entropy will be  $k \log (N!)$  greater than for a gas consisting of nothing but equal molecules. For the latter we shall then have to subtract  $k \log (N!)$  from the original entropy expression. Such considerations have originally led me to the division by  $N!$  and to the formula (16).

**Physics.** — “*On interference phenomena to be expected when Röntgen rays pass through a di-atomic gas.*” By Prof. P. EHRENFEST. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of February 27, 1915).

As is known W. FRIEDRICH<sup>1)</sup> has ascertained that a beam of Röntgen rays passing through yellow wax and other amorphous *solid* substances gives interference rings on a photographic plate placed behind it. *Liquid* paraffin also gives a ring, which, however, does not represent a maximum of darkness, but an inflection point of

<sup>1)</sup> W. FRIEDRICH, Eine neue Interferenzerscheinung bei Röntgenstrahlen: Phys. Zschr. 14, (1913), p. 317.

the decrease of darkness. FRIEDRICH shortly discusses two possible explanations of the observed phenomenon.

*a.* The solid amorphous bodies may be imagined as built up of small crystals. The interference spots of the different individual bodies uniformly turned in all directions unite on the photographic plate to rings.

*b.* For the solid amorphous substances and particularly of the liquids is "die Anordnung der Teilehen eine vollkommen regellose". In the case of the passage of Röntgen rays through such an amorphous medium we should meet with a phenomenon analogous to that of the passage of rays of light through a glass plate strewn with lycopodium powder.<sup>1)</sup>

FRIEDRICH cites the circumstance that also for liquid paraffin an interference ring occurs, in favour of the second explanation, and he therefore expresses the supposition that here we should have to do "mit Beugung am Molekül resp. Atom".

E. HUPKA<sup>2)</sup> tries, if I have understood him correctly, to give another explanation, in which the mean distance of the molecules is decisive as "grating constant".

A trustworthy introduction of statistical considerations on which the calculation of the dark rings must rest, does not seem easy to me even for liquids on account of the compact arrangement of the molecules and particularly on account of the unknown complexes (association) of adjacent molecules.

I may be therefore allowed to point out briefly that the problem is considerably simpler in case of transition of Röntgen rays *through a di-atomic gas*. Whether the *experimental* difficulties can be surmounted, I cannot judge; in case this should be so, some new data might be obtained in this way on the situation of the atoms in the gas molecule.

§ 1. Let homogeneous plane Röntgen rays fall on an isolated di-atomic gas molecule. Both atoms emit secondary waves which interfere in the whole space. We consider the interference in an arbitrary point *P* of a plane *E* (photographic plate), which lies normal to the direction of incidence of the Röntgen ray at the distance *D* behind the molecule. *D* may be considered as infinitely great with

<sup>1)</sup> DRUDE, Optik I, Afd. Kap. IV; M. LAUE, Beugungserscheinungen an vielen unregelmässig verteilten Teilehen. Sitzber. d. preuss. Akad. 1915.

<sup>2)</sup> E. HUPKA, Die Interferenz der Röntgenstrahlen Samml. Vieweg, Heft 18 (1914), p. 62.

respect to the central distance  $a$  of the two atoms of the molecule, which are supposed to be equal for the sake of simplicity.

If consecutively the molecule axis is given all possible directions by the molecule being turned round one of the two atoms  $A_1$ , the phase difference with which the secondary waves of  $A_1$  and  $A_2$  interfere in the point  $P$  changes, hence the intensity of the radiation there.

We calculate the *mean* intensity in the point  $P$  and inquire: *in what way does this mean intensity vary with the situation of  $P$  on the plate  $E$ ?*

For reasons of symmetry the mean intensity is of course the same for all those points  $P$  for which the direction molecule  $\rightarrow$  point  $P$  forms the same angle  $q$  with the direction of incidence of the Röntgen rays. With increase of  $q$  the mean density however changes oscillatorily namely as:

$$1 + \frac{\sin 2\pi q}{2\pi q} \dots \dots \dots (1)^1$$

if

$$q = \frac{2a}{\lambda} \sin \frac{q}{2} \dots \dots \dots (2)$$

[ $\lambda$  is the wavelength of the Röntgen rays;  $a$  the distance of the two atoms (supposed as points<sup>2</sup>) from each other].

The consecutive maxima and minima of (1) are in the following ratio to each other<sup>3</sup>):

$$2 : 0,78 : 1,13 : 0,91 : 1,07$$

and lie at:

$$2\pi q = 0; 4,49; 7,72; 10,90; 14,07.$$

$\frac{a}{\lambda}$	$q_0$	$q_1$	$q_2$	$q_3$
$\frac{1}{2}$	0°	90°	—	—
1	0	41	71°	114°
2	0	21	34	50
3	0	14	22	32

<sup>1</sup>) See appendix.

<sup>2</sup>) It is convenient to confine ourselves for the present to this schematisation, till experiment shall give an indication for possibly necessary refinement of the scheme.

<sup>3</sup>) Comp. the tables for  $\frac{\sin X}{X}$  in JAHNKE u. EMDE. Functionentafeln.

The preceding table gives the corresponding values of  $q$  for different values of  $\frac{a}{\lambda}$ .

§ 2. Instead of a single di-atomic gas molecule now a whole gas mass is irradiated; the dimensions of the irradiated quantity, however, will be comparatively small compared with the distance between the gas and the photographic plate  $E$  (e.g. 1 mm. to 5 cm.).

We state <sup>1)</sup>:

*The dark rings on the photographic plate will then — except for a slight diminution in sharpness — continue to be represented by equation (1).*

The decrease of sharpness corresponds with the slight changes in situation and size, which the rings (1) undergo when the centre of the molecule discussed in § 1 is made to pass consecutively through all the points of the small irradiated region.

§ 3. In the experimental realisation of these rings we are confronted with difficulties which are indeed very great, but yet possibly not insurmountable.

1. The probably very slight intensity of the whole secondary radiation. In any case we shall choose vapours the atoms of which will be as heavy as possible <sup>2)</sup>.

2. The incident radiation must be as homogeneous as possible or anyway possess such a distribution of intensity in the spectrum that at least the first ring does not fade away entirely. In order to be still able to calculate  $a$  in the latter case from the distribution of light and dark, the spectrum distribution must be known from interference figures for crystals.

3. If the first ring is to fall on favourable values of  $q$ ,  $a : \lambda$  must certainly be greater than one (see the table in § 1).

4. Possibly the dark rings that originate from the amorphous glass vessel in which the vapour is contained, might be troublesome <sup>3)</sup>. Then we should have to replace the amorphous glass e.g. by mica.

#### A P P E N D I X.

The secondary waves which two atoms  $A, B$  send to a definite

<sup>1)</sup> See appendix.

<sup>2)</sup> Or perhaps solutions; but here the phenomena are theoretically more complicated.

<sup>3)</sup> They have not occurred in FRIEDRICH's experiments with yellow wax.

point  $P$  of the photographic plate, give at that place conjointly the disturbance of equilibrium

$$M \sin p (t - \tau_A) + M \sin p (t - \tau_B) . . . . . (a)$$

The time average of the square of (a), — taken over a period, is:

$$\frac{M^2}{2} [1 + 2 \cos p (\tau_A - \tau_B) + 1] = M^2 [1 + \cos p (\tau_A - \tau_B)] . (b)$$

If the two atoms  $A, B$  belong to *different* molecules of the gas, the quantity  $\cos p (\tau_A - \tau_B)$  assumes equally often equally large positive and negative values during the time of exposure in consequence of the independent movement of the molecules, so that here the time average of  $\cos p (\tau_A - \tau_B)$  becomes zero.

It is different with two atoms belonging to *the same* molecule. We split up here the taking of the time average into two phases: *I.* All possible orientations of the axis of the di-atomic molecule, one atom being fixed. *II.* Repetition of this average value determination for all possible situations of that atom inside the (irradiated) gas space.

*Mean value determination I.*

Let  $CA$  be an incident Röntgen ray,  $AD$  the secondary ray that travels from atom  $A$  to the point  $P$  of the photographic plate. What is the locus of all the situations of the atom  $B$ , for which the difference of path

$$CDA - EBF = \Delta$$

has one and the same value? <sup>1)</sup> Answer: Describe round  $A$  a sphere with radius equal to the fixed distance of the atoms  $AB = a$ . Intersect this sphere with the plane  $B'YB$ , which is normal to the plane of drawing  $C'AD$ , and parallel to the straight line  $AU$  <sup>2)</sup>. The circle  $BB'$  along which this plane intersects the sphere is the required locus; for all its points:

$$EBF = E'B'F'.$$

Hence all of them give one and the same difference of path with respect to  $CAD$ , which can also be represented by

$$\Delta = XYZ - CAD$$

finally also by

$$\Delta = VAW = 2 (AY) \sin \frac{\varphi}{2} . . . . . (y)$$

<sup>1)</sup>  $AB$  is so small compared with  $AP$  and  $BP$  that  $AP$  and  $BP$  may be considered as parallel, hence  $\Delta$  as the difference of path with which the secondary waves from  $A$  and  $B$  arrive in  $P$ .

<sup>2)</sup> A mirror parallel to the plane  $B'YB$  would just reflect the rays  $EB', YX, EB$  in the direction  $B'F', YZ, BF'$ .



$$\frac{2ap}{c} \sin^2 \varphi = 2\pi\varrho$$

is put for shortness.

Thus we get the dark rings:

$$M^2 \left( 1 + \frac{\sin 2\pi\varrho}{2\pi\varrho} \right)$$

which were mentioned in § 1<sup>1)</sup>.

#### *Determination of the mean value II.*

The distances from Röntgen tube to molecule, and from molecule to photographic plate being enormously large in comparison with the distance  $AB=a$ , we could act up to now as if we had to deal with an interference problem of FRAUNHOFER. If for the determination of the mean value II the molecule is made to occupy all situations in the irradiated space, these molecule displacements are practically still infinitesimal compared with the distance from Röntgen tube, but not compared with the distance from molecule to plate. In connection with this in the slight displacements of the molecule *parallel* to the photographic plate the dark rings move over an equally large distance. In displacement *normal* to the plate a slight enlargement or diminution of the rings occurs. We see that this brings about a slight fading of the rings.

**Geology.** — “*On the granitic area of Rokan (Middle-Sumatra) and on contact-phenomena in the surrounding schists.* By Dr. H. A. BROUWER. (Communicated by Prof. G. A. F. MOLENGRAAFF).

(Communicated in the meeting of June 27, 1914).

Between Rokan and Loeboek Bandhara the Rokan Kiri cuts a granitic mass of about  $4\frac{1}{2}$  km. in width, which on its northwestern and southeastern sides is adjoined by tertiary sandstones and conglomerates, which however, along a portion of the south west limit, are separated from the granite by a narrow strip of schists.

During the exploration of this area some facts were collected concerning the various facies of the granites and the contactphenomena in the surrounding schists. The schists dip towards the granitic mass

<sup>1)</sup> The factor  $M^2$  varies of course also with  $\varphi$ ; perhaps in the same way as  $\cos^2 \varphi$ . In § 1 we have however disregarded this variation for the present to get a first survey.

the strike chiefly being W.N.W. to N.N.W., and the dip alternating between north east and south west; the sandstones and conglomerates which unconformably overlie the schists and the granite, and are far younger, dip away from the granite-mass on both sides.

In his description of a portion of the Western Coast of Sumatra

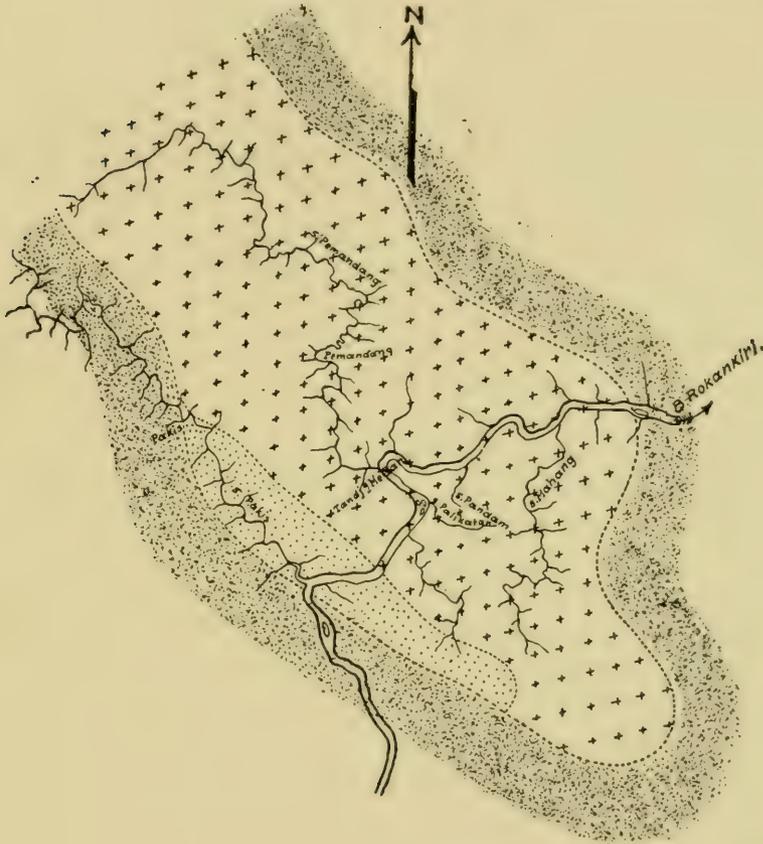
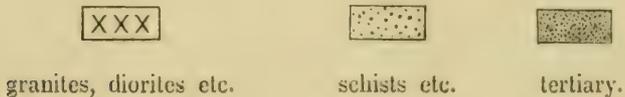


Fig. 1. Map of the granitic mass of the Rokan-county (after the map in the "Jaarboek van het Mijneuzen in Nederlandsch Indië" for 1902, made under the supervision of the engineer E. A. NEEB). Scale 1 to 100,000.



Fig. 2. Intersection over the middle of fig. 1.



VERBEEK<sup>1)</sup> describes numerous quartz diorites, which probably form irregular patches in the granites and some veins of quartz diorite in granitite. In the granitic area of the Rokan county granitic veins occur in quartz-dioritic rocks and thus a part of the granites must be younger than the quartz diorites.

#### FACIES OF THE GRANITES.

The rocks of the granitic area which were examined contain two-mica granites, biotite granites and their transitions into quartz-diorites. The quartz-diorites examined are rich in biotite and contain a green amphibole in small quantities.

Porphyritic rocks with very large feldsparphenocrists are very numerous, just as in the Malakka granites. Often the phenocrists show a more or less distinct parallel arrangement, and the porphyritic rocks sometimes occur in alternating layers with the normal ones. Rocks with gneissoid structure also occur.

Pegmatitic facies are very numerous. Along both borders of the Rokan Kiri and in the numerous side-rivers of the Rokan Kiri running through the granitic area, their outcrops are repeatedly visible as more or less irregularly defined masses or as veins running regularly for some distance; as a rule, these rocks are rich in tourmaline. In the rocks Batoe Kandik projecting on the right side of the Rokan Kiri pegmatites are found containing very much biotite, their crystals measuring sometimes several cm<sup>3</sup>, and for the rest consisting chiefly of feldspar, quartz and tourmaline. Dykes of quartz tourmaline rocks free from feldspar also occur here; the rock which intersects these pegmatites is a medium grained granite without phenocrists. The rock which protrudes at the mouth of the Sei Mahang in the middle of the Rokan Kiri shows a great variety of rocks. Along with medium-grained granites one finds here very many pegmatitic segregations which for the greater part consist of feldspar, quartz, tourmaline with dark or light-coloured mica, whereas patches with the structure of graphic granite protrude as knobs from the surrounding rock.

Dykes which are more acid and contain fewer dark minerals than the rocks they intersect were found in several places. To quote one instance dykes of light-coloured biotite granite on various points cut through quartzdiorites on both borders of the Rokan Kiri.

<sup>1)</sup> R. D. M. VERBEEK, *Topographische en geologische beschrijving van een gedeelte van Sumatra's Westkust*, 1883, p. 220.

*Biotitic granites.*

A biotitic granite of the right border of the Rokan Kiri near Tanah Dingin contains besides orthoclase some microcline and very little acid plagioclase. Quartz is found in large quantities and shows the aggregate polarisation or undular extinction commonly occurring in the granite quartzes of strongly folded regions. Muscovite only occurs in very small quantity in this rock; ore and apatite are both present. The two last mentioned minerals are often intergrown with biotite.

Similar biotite granites have been collected on the left border of the Rokan Kiri, in the sharp bend downstream from Tandjong Medan. Granophyric intergrowths of quartz and feldspar were found here in small quantities.

According to ABENDANON, green augite occurs in granites rich in biotite from the upper part of the Sei Pemandang. (Cf. "Jaarboek van het Mijneuzen" for 1902, p. 138.)

*Two-mica-granites.*

The medium-grained rocks in which the numerous pegmatites of the Batoe Kandik occur, belong to this group. They are poor in dark constituents and consist chiefly of orthoclase, some microcline and acid plagioclase and quartz. Brown as well as green biotite occur, often intergrown in one crystal and in alternating layers. Small quartz crystals are sometimes poikilitically enclosed by the feldspars; the feldspars are slightly sericitized. In these rocks again, the quartz shows aggregate polarisation and undular extinction. Ore and apatite occur in very small quantities only.

In the medium-grained rocks with the numerous pegmatites from the cliffs near the mouth of the Sei Mahang the percentage of plagioclase has increased, whereas muscovite is found in smaller quantities than biotite. Besides orthoclase some microcline is found. The plagioclase has almost the constitution of oligoclase-albite, the quartz shows aggregate polarisation, small rounded crystals of quartz are sometimes poikilitically enclosed by the feldspars. Some of the feldspars are feebly sericitized, whereas larger muscovite crystals more or less in parallel position one to the other are sometimes enclosed.

Medium-grained granites very poor in mica minerals protrude as rocks in the bed of the Rokan Kiri near Tandjong Medan.

*Quartzdiorites.*

These rocks contain less quartz and generally more biotite than the granites described above.

From the first rocks in situ on the left bank of the Rokan Kiri, in the sharp bend downstream of Tandjong Medan, and from the rocks projecting there from the right bank specimens of dioritic rocks were collected consisting chiefly of plagioclase with quartz and biotite, the further constituents being amphibole, titanite, apatite, some chlorite and very little ore.

The plagioclase has almost the same composition as andesine, some more acidic mixtures (oligoclase-andesine) also occurring, and a feebly zonal structure with repeated alternations of zones more acidic and more basic being rather common. Exceptionally the plagioclase was found to be partly surrounded by a narrow margin of granophyric texture in which the feldspar is not polysynthetically twinned. In slides of the symmetrical zone of the plagioclase this last feldspar shows a straight extinction, this fact pointing to orthoclase. The quartz shows aggregate polarisation, the lamellae of the plagioclases being bent. The biotite with very small axial angle is as a rule fresh, exceptionally some alteration into chlorite occurs. Green amphibole is found in small quantity, titanite occurs in grains and in more or less rounded crystals, and, as well as the apatite, is often enclosed by biotite. On the other hand small biotite crystals in places are enclosed by a large crystal of titanite.

*Granitic dykes in the diorites.*

At a distance of about 2 m. from each other on the left bank of the Rokan Kiri in the sharp bend down Tandjong Medan two dykes were found cutting the quartz diorites. These medium to fine-grained rocks, light coloured, consist largely of orthoclase (and microcline) and quartz. Acid plagioclases are found in small quantity, the further constituents being: biotite, apatite, and some green chlorite. Ore is almost totally absent. The chlorite is sometimes found alternating in layers with biotite in the flakes of the latter mineral. An intergrowth of kalifeldspar with quartz is remarkable in which numerous small rounded or almost idiomorphic crystals of quartz enclosed by the feldspar extinguish at the same time.

Granophyric intergrowths, in which the quartz is irregularly shaped, also occur in small quantities.

One of the granitic dykes in the quartz diorites on the other bank of the Rokan Kiri consists entirely of a mixture of quartz and feldspar, some traces only of biotite and chlorite occurring.

*Gneissoid granites.*

In a left branch of the Pakis river, near the kampong Pakis,

porphyritic rocks were found showing a distinct parallel structure and containing only few dark constituents. They are poor in plagioclase, microcline occurring in varying quantity with orthoclase. The feldspars only occur as phenocrists, as a rule rounded and showing more or less irregular contours; they show traces of sericitization and sometimes enclose rather large crystals of colourless mica. The biotite sometimes contains ore in numerous disseminated minute crystals and often it is partly chloritized.

Pyrite occurs in rather numerous small crystals in some of these rocks. Feldspar and quartz are sometimes granophyrically intergrown. The crystals of the groundmass are often found enclosed by the phenocrists of feldspar and the matrix sometimes penetrates into the phenocrists. The often occurring irregular extinctions of the quartzes point to pressure after the crystallization of the rocks.

### *Pegmatites.*

Some provisional facts will be given here on the constitution of the very numerous pegmatites. The pegmatites rich in biotite, from the Batoe Kandik, consist chiefly of plagioclase, orthoclase, quartz with undular extinction and biotite, tourmaline and colourless mica also occurring. The plagioclase has almost the constitution of oligoclase, whereas more acid mixtures approaching to oligoclase-albite, also occur. As a rule, the tourmaline shows absorption colours of brownish hue, more bluish colours sometimes being found round the brown colours as a bordering zone of varying breadth and occasionally missing; no sharp distinction exists between these varieties.

A dyke of a width of about 2 metres with N. N. W. strike, consisting of pegmatite containing tourmaline and occasionally much biotite, in which numerous small crystals of reddish brown garnet are macroscopically visible, over a short distance appears outcropping in small rocks, which, the level of the water being low, are visible on the left bank of the Rokan Kiri near Tandjong Medan. They are rich in acid plagioclase, orthoclase and quartz. Several of the plagioclases proved on examination to be acid oligoclase-albite, more basic mixtures, however, also occurring. The feldspars sometimes are to some extent sericitized. The crystals of the garnet are idiomorphous and microscopically colourless. The tourmaline is usually not idiomorphous in the prismatic zone, the brown colour of the crystals is often less deep in the central parties than in the bordering zone, more blue colours moreover occurring in the central parts. Finally, the occurrence of zircon in small idiomorphous crystals with pyramidal limit outlines must be mentioned.

: In the small rocky isle near the mouth of the Sei Mahang, pegmatites with much dark or light coloured mica are almost similarly constituted as the surrounding granites; the feldspar crystals measuring up to ten decimeters, found at the same place, which are beautifully graphic-granitically intergrown with quartz, have been mentioned above.

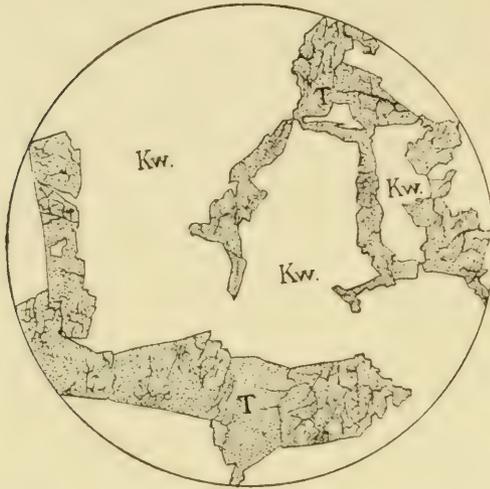


Fig. 3. Concretion of one quartz and one tourmaline crystal.

T = tourmaline. Qu. = quartz.

consequently belong to the same crystal. The tourmaline chiefly shows brown absorption colours, more bluish colours sometimes occurring in the bordering zones; a blue tourmaline is occasionally crystallized in small crystals at the periphery of the brown crystals. In these pegmatites as yet no tin-ore was found; about the same thing is reported by TOBLER<sup>1)</sup> from the granites of the mountains of Doeablas in Djambi, which as well as the granite of the Rokan-county are closely related to the tin-granites of Banka and Malakka. Numerous pneumatolytic veins consisting of quartz and tourmaline are found there.

#### THE SURROUNDING SCHISTS.

The schists which separate the granites along a portion of their southwestern limit from the tertiary sandstones and conglomerates, are laid bare by denudation in several places on both borders of the Rokan Kiri, and they can be excellently observed on the banks of the Sei Pakis, which crosses the whole length of the strip of schists northwest of the Rokan Kiri.

<sup>1)</sup> A. TOBLER. Voorloopige mededeeling over de geologie der Residentie Djambi. Jaarb. v. h. Mijnwezen in Ned. Oost-Indië, 1910; Verhandelingen, p. 20.

So far as they do not show any traces — or to a slight degree only — of contact-metamorphism, they are of small mineralogical importance; the contact-rocks only will be mentioned underneath.

Many of the rocks contain calcite in varying quantity, and the series of rocks examined includes various gradations between limestone, sericite schist, and chert or quartzitic schist free from calcite and sericite. Limestones are e.g. exposed for a great distance in the *S<sup>ei</sup> Mangis*, a small right branch of the *S<sup>ei</sup> Pakis*, about halfway between the kampong Pakis and the Rokan Kiri. Those are partly white semi-crystalline limestones, partly they are very dark coloured or rich in strongly pigmented veins. Farther upstream in the river Mangis these rocks are covered by the tertiary sandstones and conglomerates.

Transitions of these rocks into phyllites rich in calcite by intermedianece of rocks with little quartz and sericite in a calcitic matrix are found; whereas by an increase of the percentage of quartz and mica, transitions into the calcium-phyllites are formed. Calcium-phyllites with sericite schists are e.g. exposed in the banks of the *S<sup>ei</sup> Pakis* near its mouth, and higher upstream in the river similar rocks alternating with rocks richer in calcite and with limestones are repeatedly exposed. The sericite schists are sometimes macroscopically dense rocks, sometimes they are crystalline and strongly schistose. The latter often contain tourmaline, whereas also varieties rich in pyrite are found.

The tourmaline is often more or less idiomorphous in the prismatic zone, sometimes the crystals being divided into various irregular, simultaneously extinguishing parts, separated by the quartz-sericite-mixture.

The quartz shows aggregate polarisation and undular extinction, kataklastic structures often occurring.

Fine-granular and strongly schistose two-mica-schists containing much mica which are found in the left bank of the *S<sup>ei</sup> Pakis*, contain some tourmaline and pyrite, and moreover in lenticular portions which are poor in mica or free from mica some feldspar was found in small quantity between the quartz crystals. This fact in connection with the high percentage of biotite and with the facts to be mentioned underneath, renders it probable that these rocks have already to a certain degree been affected by contact-metamorphism.

Finally the occurrence of brecciated rocks may be mentioned containing fragments of sericite schists cemented by a fine aggregate of quartz grains. In these sericite schists black layers strongly pigmented alternate with those containing little pigment.

## CONTACT-PHENOMENA.

Although in consequence of the fact that little rock in situ is exposed, not a continuous section is found from the granite area into not contact-metamorphic rocks, the character of the metamorphism may sufficiently be determined from the facts collected.

Between the kampong Pakis and the northwestern side of the strip of schists, in the middle of the river, two little rocks arise, consisting partly of granite, partly of contact-metamorphic rocks. At the same place, in the right bank of the river, granitic rocks of distinctly parallel structure are exposed.

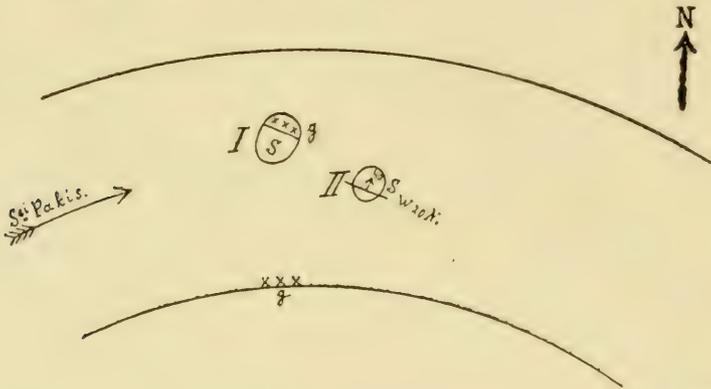


Fig. 4. Contact of granite and schists a short distance upstream from kampong Pakis.

(g = granite. S = hornfels etc. cut by apophyses of granite.)

The northern portion of the small rock I is composed of granitic rocks, the southern portion as well as the rock II consisting chiefly of hornfels with intercalated apophyses of igneous origin. The granites are dark coloured; they contain much biotite and show distinctly parallel structure. The rocks are altered into a hard, fine crystalline grayish-black hornfels, showing the original schistosity of the unaltered sediments. Very thin layers of granitic material can be distinguished even macroscopically.

Microscopically the hornfels and the intercalated granitic bands do not show sharp lines of demarcation.

The granite from the northern portion of rock I consists of orthoclase, plagioclase, quartz, biotite, some ore, zircon and apatite. The feldspars form larger crystals, enclosed by a finer quartzose crystalline mixture containing feldspar and other minerals. The rocks therefore show a more or less distinct porphyritic structure with a subordinate groundmass. The plagioclases belong to the andesine

group; in some slides, a.o. from the extreme northern end of rock I they show a zonal structure with a bordering zone of great acidity. Sometimes the crystals have been broken and the different fragments have been shifted with respect to each other, and later a greenish mica substance has been deposited in the cracks. The flakes of biotite also are often bent and show strongly undular extinctions; the quartz, found in great quantity in the groundmass, shows a strong aggregate polarisation. The cliff on the right bank of the *Sei Pakis* near the rocky islands, contains rather large plagioclase and orthoclase crystals in the quartzose mixture of quartz, feldspar and biotite. Various plagioclases were determined to be andesine, they often show a zonal structure with more acidic bordering zone. Along the circumference of the feldspar crystals a granophyric texture is found in places. The rock contains rather much calcite, and also some crystals of zircon.

The contact-metamorphic sediments alternate with numerous layers of granitic rocks, several similar layers — sometimes macroscopically, sometimes only microscopically observable, — also occurring in the hornfels. Thus it is a case of injection of granite in the schists, whereas between the stratified granitic apophyses the schist moreover has been feldspathised independently of the development of the feldspars in the granite.

Granitic apophyses in the island II principally consist of orthoclase and of, sometimes zonal, plagioclase, quartz and biotite. The feldspars occur as crystals of good size, more or less rounded and sometimes strongly sericitized, enclosed by a fine-grained granular mixture of quartz and biotite with well marked strongly schistose structure.

The quartz shows a strong aggregate-polarisation. Further these apophyses contain rather much brown or greenish brown tourmaline, some pyrite and a few small crystals of zircon<sup>1)</sup>, which sometimes show rounded forms, sometimes are idiomorph, with pyramidal limitation. The hornfels differs from the granite of the apophyses with regard to the size of grains and the mutual relation of constituting minerals. They are very schistose, rich in biotite, often contain tourmaline too, and show a more or less distinct porphyritic structure caused by the large size of several of the feldspar crystals. The feldspars are free from inclusions, or they include a few quartz crystals and flakes of biotite only. In some metamorphic rocks apatite is found in numerous crystals.

<sup>1)</sup> These crystals are colourless and often show pyramidal limitation. In basal intersections we sometimes meet with distinct cleavage lines according to (110). As yet no cassiterite has been demonstrated to be present in these rocks.

Very schistose hornfels in the same island the layers of which dip away beneath the rocks mentioned above consist almost entirely of feldspathised schists with intercalated layers of granitic material which are very thin and partly can only be observed under the microscope. In this hornfels too, larger feldspars contrast with the fine crystalline quartz-biotite-mixture surrounding the feldspars. Here also, inclusions of quartz and biotite occur in small number in some feldspars, sometimes being arranged in the direction of schistosity. Exceptionally and in a small number, these inclusions also occur in a hornfels near the contact with the granites in the little island I, and here too a more or less distinct arrangement parallel to the schistplanes of the rock can be observed; however, for far the greater part the feldspars are totally free from inclusions. Moreover, this rock is much coarser crystalline than those mentioned above. Some larger feldsparcrystals occur in the finer crystalline mixture. The structure of the hornfels is very much like that of the adjoining granite rocks and no sharp line of demarcation exists between the two kinds of rocks.

Further away from the contact, metamorphic rocks were collected in which much muscovite is present along with biotite.

In the southern part of the island II, similar granitic rocks as in the northern part of the island I occur; here the feldspars are very strongly sericitized and the rock contains much secondary calcite; numerous pyritecrystals also occur. Adjoining these granites, but dipping away from the granite with strike W. 20 N. and dip  $40^{\circ}$  N.E. dense cherts and sericite-schists occur, which on microscopical examination prove to consist of a very fine-grained mixture of quartz-crystals and aggregates of small quartz-grains. In the quartz-mixture sericite occurs in varying quantity; along with sericite, chlorite, iron-ore and some apatite occur. These rocks show no traces of contactmetamorphism.

Rather well crystallized muscovite schists in the banks of the Sei Pakis have been mentioned above.

Not far downstream from the kampong Pakis rocks resembling hornfels are found, in which much muscovite occurs along with biotite; in some of them traces of feldspathisation were observed. However, many of the rocks examined are free from feldspar; they contain a few larger quartz crystals with undular extinction, or aggregates of quartz-grains in a finer-crystalline mass chiefly consisting of quartz with biotite and muscovite.

Tourmaline crystals of idiomorphic or almost idiomorphic limitation are sometimes rather numerous, a blue core is sometimes rather

sharply separated from a brown bordering zone. Finally, small crystals of apatite and fine ore-particles occur in these rocks. In the left branch of the Sei Pakis near the kampong Pakis, the first solid rocks found in situ are granites with a parallel-structure often apparent. It is highly probable that in the part not exposed between the granites and the Sei Pakis, the zone of the feldspar hornfels and granite apophyses occurs, which farther up the river is exposed. The granites at the contact contain much biotite, the increase of the percentage of biotite being a common phenomenon of endomorph contact-metamorphism. This fact may here account for the high percentage of mica, although elsewhere in the granitic area, rocks containing much biotite also occur.

VERBEEK <sup>1)</sup> describes dark gray, sometimes black hornfels containing feldspar, from Pamoesian near the river Sinamar in the Ngalau-Sariboe mountains. The percentage of feldspar (chiefly plagioclase) is only contained in the contact-rocks just touching the granite, as soon as we get away from the granite more than 2 or 3 m., the percentage of feldspar diminishes and soon totally disappears. Apparently we have to do here with contact-phenomena equivalent to those mentioned above.

Putting together the data obtained in several localities, the following statement may be given on the nature of the contact-metamorphism.

1. At the contact of the granites a narrow zone of the surrounding schists has been feldspathised. The contact rocks almost graduate into gneisses, and the sharp contrast between igneous rock and sediment has disappeared. Granite apophyses occur in alternating layers with the schists. Farther away from the contact this feldspathisation is entirely missing.

2. In the hornfels the original stratification of the rocks has been conserved.

3. Biotite is the mica found in the feldspathised hornfels near the contact with the granite, muscovite appearing in the contact metamorphosed rocks farther away from the contact.

4. The zone of the contact rocks with Al-silicates (andalusite etc.) is missing, the zone of the mica schists succeeding the feldspathised zone <sup>2)</sup>.

5. Tourmaline is a common mineral in the contact-metamorphic rocks.

<sup>1)</sup> R. D. M. VERBEEK, loc. cit. p. 179.

<sup>2)</sup> "Knotenglimmerschiefer" and "Knotenthonschiefer" were not met with, but the author considers undecided whether they are entirely missing or not.

6. The often appearing porphyritic structure with rounded edges, of the apparent feldspar phenocrysts of the granites, and the highly undular extinctions and aggregate-polarisations of the quartz in the granites and hornrocks point to strong pressure in the rocks after they had been solidified.

This metamorphism thus shows an entirely different character from that of the classic contact-zones of the type Steiger Schiefer (ROSEN-BUSCH), where the sediments furnish the mineral constituents, the eruptive rocks heat and pressure, molecular interchanging only taking place in the contact-zone. It is much like the metamorphism described by MICHEL LÉVY for the Plateau Central, by BARROIS for Brittany, and by LACROIX for the Pyrenees. The feldspathisation of the schists without connection with the stratified granite apophyses, and the manifold occurrence of tourmaline, point to the influence of mineralisators and to a supply of constituents of the granitic magma in the contact-zone.

The numerous pegmatites mentioned above tend to prove that mineralisators have been present in the granitic magma in large quantities. The presence of feldspars and tourmaline as well in the pegmatites as in the contact-metamorphic rocks, illustrates the pneumatolytic character of the contact-metamorphism.

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#### E R R A T A.

In the Proceedings of the Meeting of September 26, 1914.

p. 507 in the table: in the column headed  $10^3 \angle R$  for 237 read 244.  
the numbers of the column headed  $R-1$  are to be provided with the sign —.

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April 23, 1915.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING  
of Friday April 23, 1915.  
VOL. XVII.

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

*Secretary:* Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Vrijdag 23 April 1915, Dl. XXIII).

C O N T E N T S.

- F. M. JAEGER: "On a New Phenomenon Accompanying the Diffraction of Röntgenrays in Birefringent Crystals." (Communicated by Prof. H. IIAGA), p. 1204. (With 4 plates).
- F. M. JAEGER: "Researches on PASTEUR'S Principle of the Connection between Molecular and Physical Dissymmetry." I. (Communicated by Prof. P. VAN ROMBURGH), p. 1217.
- ERNST COHEN: "The Allotropy of Bismuth" II, p. 1236.
- ERNST COHEN and W. D. HELDERMAN: "The Metastability of the Metals in consequence of Allotropy and its Significance for Chemistry, Physics and Technics" IV, p. 1238.
- P. EHRENFEST: "On the Kinetic Interpretation of the Osmotic Pressure." (Communicated by Prof. H. A. LORENTZ), p. 1241.
- W. VAN DER WOUDE: "On NÖTHER'S theorem." (Communicated by Prof. JAN DE VRIES), p. 1245.
- JAN DE VRIES: "A bilinear congruence of rational twisted quintics", p. 1250.
- JAN DE VRIES: "Some particular bilinear congruences of twisted cubics", p. 1256.
- F. A. H. SCHREINEMAKERS: "Equilibria in Ternary Systems". XVIII, p. 1260.
- A. W. K. DE JONG: "Action of Sunlight on the Cinnamic Acids". (Communicated by Prof. P. VAN ROMBURGH). p. 1274.
- C. E. B. BREMEKAMP: "On the mutual influence of phototropic and geotropic reactions in plants". (Communicated by Prof. F. A. F. C. WENT), p. 1278.
- W. DE SITTER: "On the mean radius of the earth, the intensity of gravity, and the moon's parallax", p. 1291.
- W. DE SITTER: "On Isostasy, the moments of inertia, and the compression of the earth," p. 1295.
- W. DE SITTER: "The motions of the lunar perigee and node, and the figure of the moon", p. 1309.
- A. B. DROOGLEEVER FORTUYN: "The decoloration of fuchsin-solutions by amorphous carbon." (Communicated by Prof. J. BOEKE), p. 1322.
- H. J. HAMBURGER: "Phagocytes and respiratory centre. Their behaviour when acted upon by oxygen, carbonic acid, and fat-dissolving substances. Explanation of the excitement-stage in narcosis", p. 1325.

**Physics.** — “*On a New Phenomenon Accompanying the Diffraction of Röntgen-rays in Birefringent Crystals.*” By Prof. Dr. F. M. JAEGER. (Communicated by Prof. H. HAGA.)

(Communicated in the meeting of March 27, 1915).

§ 1. A short time ago HAGA and JAEGER<sup>1)</sup> made some observations on the diffraction of RÖNTGEN-rays in crystals of *cordierite*, from very beautiful, perfectly transparent and homogeneous examples of which suitable plates were cut parallel to the three pinacoïdal faces {100}, {010} and {001}. On this occasion the RÖNTGENogram of the plate parallel to {001} of this mineral hitherto considered rhombic-bipyramidal, appeared in fact to possess two symmetry-planes perpendicular to each other, as well as a binary axis; the patterns however, obtained by the transmission of RÖNTGEN-rays through the plates parallel to {100} and {010}, appeared to possess only one single symmetry-plane. This combination of symmetry-elements is just the essential of rhombic-hemimorphic crystals.

It must be remarked however, that this fact is contrary to the consequences which follow from the theory of these phenomena, as far as it regards the expected symmetry of the RÖNTGEN-patterns.

The question, what will eventually be the symmetry of the RÖNTGENograms of crystals of a certain symmetry-class, can be answered comparatively easily. Deductions of this kind were made for the first time in 1913 by G. FRIEDEL<sup>2)</sup>, who concluded, that under *no* circumstances such symmetry of crystals, as were characterized by the absence of a centre of symmetry, could be revealed in their RÖNTGEN-patterns.

The reasoning of FRIEDEL is principally as follows. He deduces the complex of symmetry-properties which is characteristic of hemihedral and tetartohedral crystals, from those belonging to the holohedral forms, by the suppression of certain symmetry-elements in the latter groups, thereby making use of the wellknown fact, that in the holohedral crystals every plane of symmetry corresponds to a binary axis perpendicular to it. This results from the fact, that all holohedral crystals possess a centre of symmetry, and that such a centre, if combined with either a plane of symmetry or with an axis of pair period, necessarily will cause the presence of the other

<sup>1)</sup> H. HAGA and F. M. JAEGER, Proc. of the R. Acad. Amsterdam, **17**, 430. (1914).

<sup>2)</sup> G. FRIEDEL, Compt. rend. de l'Acad. des Sciences, Paris **157**, 1533, (1913).

of any of those three symmetry-elements; thus the combination of a symmetry-centre with a symmetry-plane having always the presence of a binary axis perpendicular to that plane as a consequence; and a centre combined with an axis of pair period always involving the existence of a symmetry-plane perpendicular to that axis. If now all hemihedrical and tetartohedrical crystals are considered as polyhedra, whose symmetry-groups correspond to complete secondary groups of the symmetry-complex of the holohedrical forms of the same system, then those secondary groups can be mathematically deduced from the primary groups, by suppression of definite symmetry-properties from the primary groups; from a mathematical standpoint nothing can be objected to such a way of reasoning; only it is necessary to keep always in mind, that from a *crystallogenetical* standpoint the hemi- and tetartohedrical crystalforms have of course nothing to do with the holohedrical ones.

Just because the centre, the plane of symmetry and the binary axis perpendicular to it, are always connected two and two in the way described before, it follows, that the deduction of the hemihedrical and tetartohedrical secondary groups from the holohedrical ones, can occur only by *simultaneous* suppression of *two* of them, in the symmetrygroups of the holohedrical forms. This suppression can be made in three ways:

a) So that one or more symmetry-planes + symmetry-centre are eliminated.

b) So that one symmetry-plane + a binary axis perpendicular to it are eliminated.

c) So that a binary axis + the symmetry-centre disappear.

If now in a holohedrical crystal of any system,  $S_1$  and  $S_2$  are two secondary RÖNTGEN-rays, which will be equivalent by symmetry to a certain plane  $V$ , they will also be symmetrically situated with respect to the binary axis perpendicular to the plane  $V$ ;  $S_1$  and  $S_2$  will moreover always be centrically symmetrical to themselves, because every particle of the space-lattice, if reached by the ether-motion, will start as a centre of a secondary radiation in all directions.

If now in the holohedrical form of the system we imagine the centre of symmetry suppressed, then:

in the case of a)  $S_1$  and  $S_2$  will still remain symmetrically arranged to the binary axis, perpendicular to the simultaneously disappearing plane; and:

in the case of c), they will remain symmetrical with respect to

the plane, perpendicular to the binary axis, which disappears at the same time as the symmetry-centre.

Thus in both these cases the symmetry of the RÖNTGEN-patterns will evidently remain *unchanged*; they will show the same symmetry as the RÖNTGEN-patterns of the holohedrical forms of the system would possess. From this results that all merohedrical crystals whose symmetry can be derived in the ways described sub *a*) and *c*), will give RÖNTGENOGRAMS of the same symmetry as in the case of the corresponding holohedrical crystals.

Only for the merohedrical crystals of the type mentioned sub *b*), the RÖNTGENOGRAM will possibly manifest a different symmetry, than may be expected in the case of the holohedrical forms.

The sub *a*) mentioned symmetry-groups are characteristic of all crystals, which only possess *axial* symmetry; that is to say: for all crystals of those eleven classes, whose forms are different from their mirror-images, and which can exist therefore as *enantiomorphous* polyhedra. *Thus all dextro- and laevogyratory antipodes will necessarily manifest identical RÖNTGEN-patterns.*

Furthermore to the groups derived sub *a*) and *c*) will belong all those crystals whose symmetry is that of *hemimorphic* crystals; in the latter therefore the absence of the symmetry-centre will *not* be shown by the RÖNTGENOGRAMS in any other way than in the case of crystals of other symmetry-classes.

On more detailed consideration it appears that the cause, *why* the absence of a symmetry-centre in the crystals can never be revealed in the RÖNTGEN-patterns, is to be ascribed to the fact, that the generated secondary radiation is in itself of a centrally symmetrical nature, just as in the case of ordinary light-waves. If this were *not* the case, then the symmetry of the RÖNTGENOGRAMS could be discerned in the same 32 symmetry-classes, just as with the polyhedral crystalforms themselves, which are generated under the influence of the one-sided forces of crystallisation. However it will appear that even such a supposition would not be sufficient to give an explanation of the new phenomena to be recorded here.

§ 2. The problem we have had before us for a long time, and which evidently could only be answered by means of numerous experiments, was just this: what symmetry will eventually be revealed in the RÖNTGEN-patterns of all kinds of merohedrical crystals.

Originally it seemed as if the experience hitherto obtained fully supported the correctness of the above mentioned theoretical deductions.

In the RÖNTGENOGRAM <sup>1)</sup> of the *sphalerite*:  $ZnS$ , which crystallizes in the hexacistetrahedral class, *no* other symmetry could be stated than that which corresponds to the hexakis-octahedral crystals.

On the other hand there is certainly another symmetry present in the case of *pyrite* <sup>2)</sup>:  $FeS_2$ , which belongs to the dyacisdodecahedral class, and which possesses thus a centre of symmetry.

The right-handed and left-handed rotating crystals of *sodiumchlorate*:  $NaClO_3$ , gave, on transmission of a pencil of RÖNTGENRAYS, *identical* patterns (Table I, fig. 1 and 2), which, if the plates were parallel to the faces of the cube, were of the same apparent symmetry, as the images of the pyrite, — just as EWALD and FRIEDRICH <sup>3)</sup> have also stated. It can be easily shown, that the same crystal (dextrogyratory), if radiated through perpendicularly to each of the cube-faces, always gave the same image, absolutely corresponding with that of a laevogyratory crystal, under the same conditions of experiment. Thus the absence of a symmetry-centre in this case could *not* be stated; both the symmetry-planes, perpendicular to each other, which in the case of the pyrite can be attributed to the crystals themselves, appear here in the RÖNTGENOGRAM, because the symmetry-centrum of the radiation is superimposed on the symmetry of the chlorate-crystals, which symmetry is characterised by the presence of only three perpendicular binary axes and the four ternary ones <sup>2)</sup>.

According to FRIEDEL, plates of dextro- and laevogyratory quartz, if cut parallel to  $\{0001\}$ , will give *identical* RÖNTGEN-patterns. Just in the same way, the crystals of dextro- and laevogyratory *luteo-triethylenediamine-kobaltibromide* <sup>4)</sup>:  $\{Co(Aein)_3\}Br_3 + 2H_2O$ , which crystallizes in the tetragonal system, gave identical RÖNTGEN-patterns, showing the presence of four vertical planes of symmetry.

<sup>1)</sup> LAUE, FRIEDRICH und KNIPPING, Bayr. Ak. der Wiss. München, 303. (1912).

<sup>2)</sup> It is remarkable, that the spots have not an *oval*, but a *rectangular* shape here; this fact cannot be explained in the way suggested by BRAGG, by the incomplete parallism of the incident rays of the pencil. Such phenomena were observed likewise with some other crystals, so e.g., with *sylvine* ( $KCl$ ), perpendicular to the ternary axis. With *sylvine* also perpendicular to a quaternary axis the rectangular spots were observed; moreover the central spot here shows a radiation in eight directions, parallel to the faces of the rhombusdodecahedron, a phenomenon quite unexplicable at this moment. As to the rectangular shape of the spots, we are persuaded now that it is principally connected with the thickness of the crystalplates: the phenomenon manifests itself only in the case of thick plates, being more prominent, if the plate is thicker.

<sup>3)</sup> EWALD und FRIEDRICH, Ann. der Phys. (4), **44**, 1183 (1914); vide also: FRIEDRICH, Deutsche Naturforscher und Ärzettag, Wien, (1913); BRAGG, Proc. R. Soc. London, **89** A, 477, (1914).

<sup>4)</sup> F. M. JAEGER, Verslagen Kon. Ak. Amst. April, (1915). (Still to be translated in these Proceedings).

On the other hand, in the case of the neutral *ethylsulfates of the rare earth-metals*<sup>1)</sup>, which possess hexagonal-bipyramidal symmetry, the hemihedrical structure was found to be expressed quite clearly in the RÖNTGENOGRAM, which is also in full accordance with the consequences of the theory, as this represents the case above mentioned sub *b*).

Further control of the exactness of these conclusions by experiment was finally only possible to me with the aid of the beautiful RÖNTGENOGRAMS obtained at the Physical Laboratory of this University by my friend and colleague H. HAGA with the crystallographical material especially selected by me for this purpose. Without his aid and kindness this investigation would have been quite impossible, and I therefore wish to express to him here my sincere thanks once more.

In fig. 1 the corresponding photo of the *apatite*:  $Ca_5Cl(PO_4)_3$  is reproduced in stereographical projection<sup>2)</sup>.

The plate used here was cut perpendicularly to the *c*-axis; it gave a very beautiful photographic image (Table I, fig. 3). The presence of a senary axis, but the absence of all vertical symmetry-planes is immediately recognisable here.

§ 3. For the purpose of obtaining further data of this kind, plane-parallel plates were cut from crystals of *ferric-ammonia-alum*:  $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ , and of *potassium-chromic-alum*:  $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ , — in both cases perpendicularly to a ternary axis.

In fig. 2 and 3 the patterns obtained are reproduced in stereographic projection. It is immediately evident that these images only show a ternary axis, but *no* planes of symmetry whatever. This is in full agreement with the theory: for the *alums*, just like *pyrite*, are dyacidododecahedral, and from the theoretical considerations mentioned above it follows, that they may eventually manifest their hemihedrical character in their RÖNTGENOGRAMS. But because these crystals do not possess any other planes of symmetry than those which are parallel to the faces of the cube, the image perpendicular to the ternary axis will in fact manifest no other symmetry-properties than those which follow from the mere presence of the ternary axis itself.

<sup>1)</sup> F. M. JAEGER, these Proceed. **16**, 1095. (1914); Recueil des Trav. des Chim. des Pays-Bas et de la Belgique, T. **33**, 343. (1914).

<sup>2)</sup> In all these projections, *d* signifies the thickness of the crystalplate, *A* the distance between the frontal face of the crystal plate and the sensitive film of the photographic plate.

Thus as far as experience goes, the phenomena observed in crystals of the *regular* system seem to be in all cases in full agreement with the postulations of the theory. In this connection it may here be definitely stated, that the conclusions made by HAGA and JAEGER<sup>1)</sup> some time ago, from their experiments with *boracite* above and below 400° C., are now seen to be completely justified. For boracite at room-temperature, — *if* it were really regular, — would be of hexakis-tetrahedral symmetry; and thus its RÖNTGENogram would possess just the same symmetry as that of the sphalerite; i. e. that the image would be identical with the pattern of boracite, which was obtained *above* 400° C., — because this corresponds to the holohedral symmetry of the regular system. But the image obtained by the authors at room-temperature, now only shows the presence of two perpendicular planes of symmetry and a binary axis: therefore it can only correspond either to a rhombic structure, or to a dyacisdodecahedral, or to a tetrahedral-pentagonedodecahedral crystal. The last mentioned two symmetry-groups however must be excluded definitely because of the characteristic development of the boundary forms of the boracite; thus the symmetry of the RÖNTGEN-pattern at room-temperature can only correspond to a *rhombic* arrangement of the molecules, the optical behaviour (biaxial) of the composing lamellae being in full agreement with this supposition. The internal change of symmetry of the boracite, if heated above 400° C., seems therefore to be incontestably proved by the authors in this experiment.

§ 4. If now we leave for the present out of consideration the cases of the composite pseudo-symmetrical (mimetic) crystals hitherto studied, it seems really, as if in *all* cases, where regular or uniaxial crystals were studied, the results of the experiments were in full agreement with the conclusions which necessarily follow from the now adopted theory of the said phenomena.

However, the case of the rhombic *cordierite* is in flagrant contradiction with it: for from the theory it follows immediately, that *crystals of all three classes of the rhombic system must give Röntgenograms whose symmetry corresponds to that of the holohedral forms.*

Thus plates parallel to the three pinacoidal faces: {100}, {010} and {001}, must always give patterns which are symmetrical with respect to two perpendicular planes of symmetry; their intersection, i. e. the line perpendicular to the photographic plate, must therefore in all cases be a binary axis.

<sup>1)</sup> H. HAGA and F. M. JAEGER, These Proceed. 16. 792. (1914).

If the *cordierite* therefore were really hemimorphic, even then its hemimorphy could under *no* circumstances be revealed in its RÖNTGEN-patterns in the way formerly observed by us! Notwithstanding that however, nobody can doubt the fact, that the RÖNTGEN-ograms of plates parallel to  $\{100\}$  and  $\{010\}$ , only manifest one single vertical symmetry-plane. There must be some unknown cause therefore, why the other planes of symmetry in the images have vanished.

As long as this case was the only one known, it was allowable to regard it as quite accidental.

*The following experiments however carry the conviction, that the theoretical views demonstrated in the beginning of this paper, are quite insufficient to explain the phenomena, as soon as they are studied in biaxial crystals, instead of in optically isotropous or uniaxial crystals, radiated through parallel to their optical axis.*

The nature of these deviations may be seen from the facts described further-on; it will however be adviceable first to say something more in connection with the RÖNTGEN-ograms of some uniaxial crystals, from which plates cut perpendicularly to the optical axis were studied.

*Turmaline* is ditrigonal-pyramidal; according to the above mentioned theory the RÖNTGEN-pattern must show the same symmetry as *calcite*, which is of ditrigonal-scalenohedrical symmetry. Just in the same way the pattern of the strongly dextrogyratory *cinnabar*: *HgS*, which crystallizes in the trigonal-trapezohedrical class, should manifest the same symmetry.

Indeed, it can be seen from fig. 4 and 5, — which represent in stereographical projection the RÖNTGEN-patterns, obtained with plates perpendicular to the optical axis, — that these images do not only possess a ternary principal axis, but moreover three vertical planes of symmetry; and they thus really show the same symmetry in their RÖNTGEN-ograms, as the *calcite*.

From this it follows immediately, that e.g. the images for dextro- and laevogyratory *cinnabar*, if radiated through perpendicularly to the basal face  $\{0001\}$ , must be quite *identical*.

In Plate I fig. 4 the original photograph for *turmaline* is reproduced. Whether crystalplates of these minerals, when parallel to  $\{\bar{1}2\bar{1}0\}$  will now really show the presence of a binary axis in their RÖNTGEN-ograms as follows from the theory, we have yet to find out by more numerous experiments<sup>1)</sup>. But in any case we can say,

<sup>1)</sup> Really we have found now this conclusion confirmed by experiment, as will be published in a short time.

that if these crystals are radiated through in a direction, in which they are *optically-isotropous*, hitherto nothing could be found which indicated a divergence between the theory and the experiments.

§ 5. Quite different however are the phenomena observed in the cases of biaxial crystals, i.e. of such crystals, which are birefringent in *all* directions, and in which therefore the anisotropy of the ether will manifest itself in *all* directions.

In order to study the simpler cases first, we started with crystals of *rhombic* symmetry. Plates were cut from them going exactly parallel to the three pinacoidal faces:  $\{100\}$ ,  $\{010\}$  and  $\{001\}$ . It might be expected therefore, that every image would appear symmetrical with respect to a pair of perpendicular symmetry-planes, while the normal on the photographic plate would be a binary axis.

The experiments were first of all made with plates of a beautiful, perfectly transparent crystal of dextrogyratory *sodium-ammonium-tartrate*:  $\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 + 4\text{H}_2\text{O}$ . The crystallographic measurements were in perfect agreement with those of RAMMELSBERG: the salt is rhombic-bisphenoidal, and thus possesses as symmetry-elements only three perpendicular binary axes, but neither a plane nor a centre of symmetry.

In fig. 6, 7, and 8 the stereographical projections of the obtained RÖNTGENOGRAMS are given; on Plate II, in fig. 5 and 6, the original photographs of plates parallel to  $\{010\}$  and  $\{100\}$  are further reproduced; they were, as in all following cases, obtained with the use of a screen "Eresco" behind the photographic plate.

Although the time of exposure was fully three hours, the impressions on the photographic plate in the case of a plate parallel to  $\{001\}$  were extremely feeble; this fact could perhaps be partially caused by the rather great distance of the spots from the centre of the plate. The characteristic symmetry towards both perpendicular planes (vid. projection fig. 8) is however immediately recognisable.

The same fact, that the transmission of the RÖNTGEN-rays is so much less effective in one direction of the crystal than that in the others, will be found in other cases also, e.g. in that of the *hambergite* which will be described afterwards.

It is immediately evident, that these results are in total disharmony with the postulations of the theory.

The stereographical projection (fig. 7) of the image obtained by transmission of the RÖNTGEN-rays in the direction of the *b*-axis (plate parallel to  $\{010\}$ ), only possesses one single plane of symmetry: there is neither a binary axis nor a symmetry-centre present. The

plane of symmetry i.e. is parallel to  $\{001\}$ . The plane of the optical axes of the crystal being parallel to  $\{100\}$ , while the  $c$ -axis coincides with the first bisectrix of negative character, it is evident, that the homologous spots are missing in the photograph which lie in the directions parallel to the  $a$ -axis, i.e. parallel to the direction of the *smaller* optical elasticity of the crystal plate.

The figure corresponding to the image of a plate parallel to  $\{100\}$  (vid. fig. 6), also possesses only one single plane of symmetry; but it is now just the plane  $\{001\}$ , which has disappeared as such, while  $\{010\}$  remains. Here we therefore miss the spots which would correspond to directions parallel to the  $c$ -axis; thus on the photograph the spots have vanished, completely or partially, which would lie in the direction of the *greater* optical-elasticity of the crystal-plate.

On the other hand the image of a plate perpendicular to the  $c$ -axis (fig. 8) shows two perpendicular planes of symmetry, as well as a binary axis; the intensity of the spots is however very feeble indeed.

It must here be remarked, that the combination of symmetry-properties observed in these three RÖNTGEN-patterns is geometrically quite impossible for the crystals themselves. The case considered is therefore again more convincing than that of the cordierite. Hence the cause of the newly discovered phenomenon can *not* be sought in the special symmetry-character of the crystals; there must be still some unknown factor, which determines the phenomenon of the unexpected disappearance of the planes of symmetry.

§ 6. As a second case of this kind we have reproduced here the RÖNTGENograms which were obtained in the same way with plates of *hambergite*.

The choice of this very rare mineral, got at *Helgearåen, Langesundford, Norway*, was made with a view to its chemical composition:  $\text{Be}_2(\text{OH})\text{BO}_3$ ; the compound being composed of the lighter elements in the periodical system, whose atomic weights are all smaller than 20. Hambergite is rhombic; its parameter-ratio is:  $a : b : c = 0.7988 : 1 : 0.7267$ . The crystals were glassy and splendidly homogeneous; they showed the forms  $\{110\}$ ,  $\{100\}$ ,  $\{010\}$  and  $\{011\}$ , and had a prismatic aspect. A perfect cleavage is present parallel to  $\{010\}$ , a good one parallel to  $\{100\}$ . The crystals are very strongly birefringent; the birefringency is about: 0.072. The plane of the optical axes is parallel to  $\{010\}$ ; the first bisectrix, which has positive character, coincides with the vertical axis. The dispersion round the first bisectrix is only feeble, with  $\rho < v$ .

In fig. 9, 10 and 11 the stereographical projections of the RÖNTGEN-

patterns obtained are reproduced. When perpendicular to the  $c$ -axis, the photograph, remained very feeble even after  $3\frac{1}{4}$  hours' exposure; in both the other principal directions however, even after much shorter exposure, the photographs were very sharp.

The plate perpendicular to the  $c$ -axis, in fact shows two normal planes of symmetry, as well as the binary axis: in the direction of

#### ERRATA.

In the paper of F. M. JAEGER: A new Phenomenon accompanying the Diffraction of RÖNTGEN-rays, etc. the following errors must be corrected:

On Table IV Fig. 10. Plate parallel (010). Read: Plate parallel (001).

Fig. 11. Plate perpendicular to the  $c$ -axis. Read: Plate parallel to the  $b$ -axis.

A comparison with the photo's 8 on Table II and 9 on Table III will also immediately make this evident.

In connection herewith, on p. 1213, in the 19<sup>th</sup> line from the top, in stead of Fig. 11 should be read: Fig. 10.

$a$ - and  $b$ -axis is only slightly different in it.

Both pinacoides  $\{100\}$  and  $\{010\}$  have thus in an optical sense about the same relation to the direction of the  $c$ -axis, and therefore we observe that the plane of symmetry parallel to  $\{001\}$  disappears on the corresponding photos. In both plates the spots which lie in directions parallel to the *greater* elasticity have thus disappeared completely, just as in the case of hambergite.

§ 7. Finally we point out the peculiarities found in the study

plane of symmetry i.e. is parallel to  $\{001\}$ . The plane of the optical axes of the crystal being parallel to  $\{100\}$ , while the  $c$ -axis coincides with the first bisectrix of negative character, it is evident, that the homologous spots are missing in the photograph which lie in the directions parallel to the  $a$ -axis, i.e. parallel to the direction of the *smaller* optical elasticity of the crystal plate.

$a : b : c = 0.7988 : 1 : 0.7267$ . The crystals were glassy and splendidly homogeneous; they showed the forms  $\{110\}$ ,  $\{100\}$ ,  $\{010\}$  and  $\{011\}$ , and had a prismatic aspect. A perfect cleavage is present parallel to  $\{010\}$ , a good one parallel to  $\{100\}$ . The crystals are very strongly birefringent; the birefringency is about: 0.072. The plane of the optical axes is parallel to  $\{010\}$ ; the first bisectrix, which has positive character, coincides with the vertical axis. The dispersion round the first bisectrix is only feeble, with  $\rho < \nu$ .

In fig. 9, 10 and 11 the stereographical projections of the RÖNTGEN-

patterns obtained are reproduced. When perpendicular to the  $c$ -axis, the photograph, remained very feeble even after  $3\frac{1}{4}$  hours' exposure; in both the other principal directions however, even after much shorter exposure, the photographs were very sharp.

The plate perpendicular to the  $c$ -axis, in fact shows two normal planes of symmetry, as well as the binary axis: in the direction of the  $a$ -axis (parallel to the plane (010)), the density of the spots seems to be greatest, but this is only slight in comparison with that of the very numerous and intense spots on both the other patterns.

When the RÖNTGENogram is perpendicular to the  $a$ -axis (fig. 9), the expected symmetry is also unmistakably present; the circles containing most spots here lie in the direction of the  $c$ -axis (parallel to the plane (010)).

The photograph however, obtained with a plate perpendicular to the  $b$ -axis manifests only one single plane of symmetry, namely that parallel to {001}. It is evident, that this combination of symmetry-properties would be also crystallographically quite impossible, and the only suitable explanation in this case is, that the plane of symmetry (parallel to {100}) has *disappeared* for some reason. Fig. 11 proves, that the above mentioned symmetry-plane is really expressed in that photo; but if the RÖNTGEN-rays are transmitted parallel to the direction of the optical normal (i.e. perpendicularly to the directions of maximum and minimum optical elasticity) evidently the spots which would be expected in the direction of *maximum* elasticity either come out in the photo not at all or only partially.

In table II moreover two of the original photographs in figs. 7 and 8 are also reproduced; they show the said phenomenon very clearly.

In the case of cordierite only the two vertical planes of symmetry were found, for plates cut parallel to {100} and {010}. In cordierite {100} is the optical axial plane, and the  $c$ -axis is the first bisectrix, and of negative character. However cordierite is a but feebly birefringent mineral (about: 0.010) and the optical elasticity in the directions of  $a$ - and  $b$ -axis is only slightly different in it.

Both pinacoides {100} and {010} have thus in an optical sense about the same relation to the direction of the  $c$ -axis, and therefore we observe that the plane of symmetry parallel to {001} disappears on the corresponding photos. In both plates the spots which lie in directions parallel to the *greater* elasticity have thus disappeared completely, just as in the case of hambergite.

§ 7. Finally we point out the peculiarities found in the study

of *benitoite*. This very beautiful mineral, which is used as a gem, and whose chemical composition is:  $\text{BaTiSi}_3\text{O}_9$ , has some importance from the mineralogical standpoint, because it has been considered by mineralogists as the only representative of the trigonal-bipyramidal, or, — with greater probability, — of the ditrigonal-bipyramidal class.

The first opinion was expressed by ROGERS<sup>1)</sup>, the last by PALACHE<sup>2)</sup>, who as a proof of the correctness of his view emphasized the presence of a form  $\{22\bar{1}1\}$  in many crystals. Later on however JEZEK<sup>3)</sup> made it probable that the ternary axis was of a polar nature, and that *benitoite*-crystals were twins with respect to the basal face  $\{0001\}$ ; by this author *benitoite* is considered to be a ditrigonal-pyramidal mineral.

Evidently the question about the real symmetry of this remarkable, enormously dichroitic mineral, is not yet settled; for that reason this object was chosen for the study of the diffraction phenomena of RÖNTGEN-rays.

We had at our disposition very beautiful pink crystals from *San Benito County* in *California*, where *benitoite* is accompanied by natrolithe and neptunite. They were flattened parallel to  $\{0001\}$ , and showed a combination of the forms:  $\{0001\}$ ,  $\{10\bar{1}1\}$ ,  $\{01\bar{1}1\}$ ,  $\{10\bar{1}0\}$  and  $\{0\bar{1}\bar{1}0\}$ . From a beautiful, homogeneous crystal three plates were prepared exactly parallel to  $\{0001\}$ , to  $\{10\bar{1}0\}$  and to  $\bar{1}2\bar{1}0\}$ . The optical investigations of the plate perpendicular to the *c*-axis, very soon proved that the crystals show only *pseudo*-trigonal symmetry, and that they are in reality not uniaxial, but biaxial, with a very small axial angle, and with positive character of their first bisectrix which coincides with the direction of the *c*-axis. In no position was the plate completely dark when between crossed nicols. On rotating the microscope-table the interference-image often showed a deformation of the central part and distinct lemniscate-shaped inner rings, as well as the transformation of the dark cross into two branches of a black hyperbola; the plane of the optical axes is evidently perpendicular to  $\{10\bar{1}0\}$ , with the *c*-axis as the direction of the first bisectrix, which has a positive character. The birefringence of the mineral is strong; in basal sections local disturbances of the image are also observed, suggesting at once the *mimetic* character of the

<sup>1)</sup> ROGERS, *Science*, **28**, 676, (1908).

<sup>2)</sup> PALACHE, *Amer. Journ. of Science*, **27**, 398, (1909).

<sup>3)</sup> JEZEK, *Bull. intern. de l'Acad. des Sciences de Bohême, Prague* (1909). Vide also on *benitoite*: LOUDERBACK. *Publ. of Calif. Univ.* **5**, 9, 149, (1907); KRAUS, *Science* **27**, 696, 710, (1908).

A NEW PHENOMENON, ACCOMPANYING THE DIFFRACTION OF RÖNTGEN-RAYS  
IN BIREFRINGENT CRYSTALS.



Fig. 1.

*Dextrogyraty Sodiumchlorate*. Plate parallel to (100).  
 $d = 2.95$  m.M.;  $A = 45.8$  m.M.

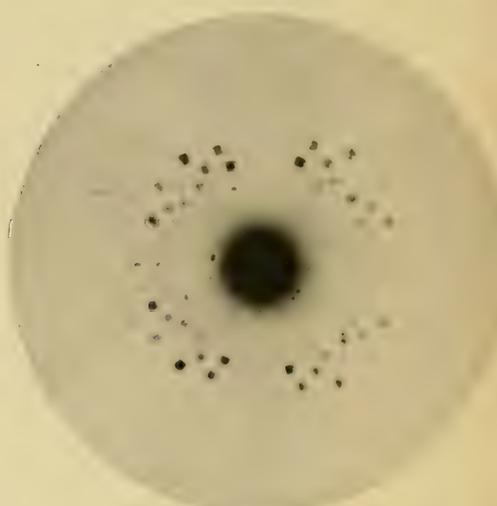


Fig. 2.

*Laevogyraty Sodiumchlorate*. Plate parallel to (100).  
 $d = 2.25$  m.M.;  $A = 45.7$  m.M.



Fig. 3.

*Apatite*; plate perpendicular to the  $c$ -axis.  
 $d = 1.5$  m.M.;  $A = 43$  m.M.

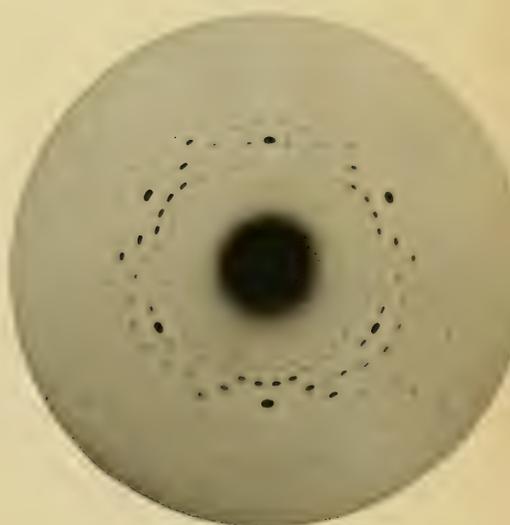
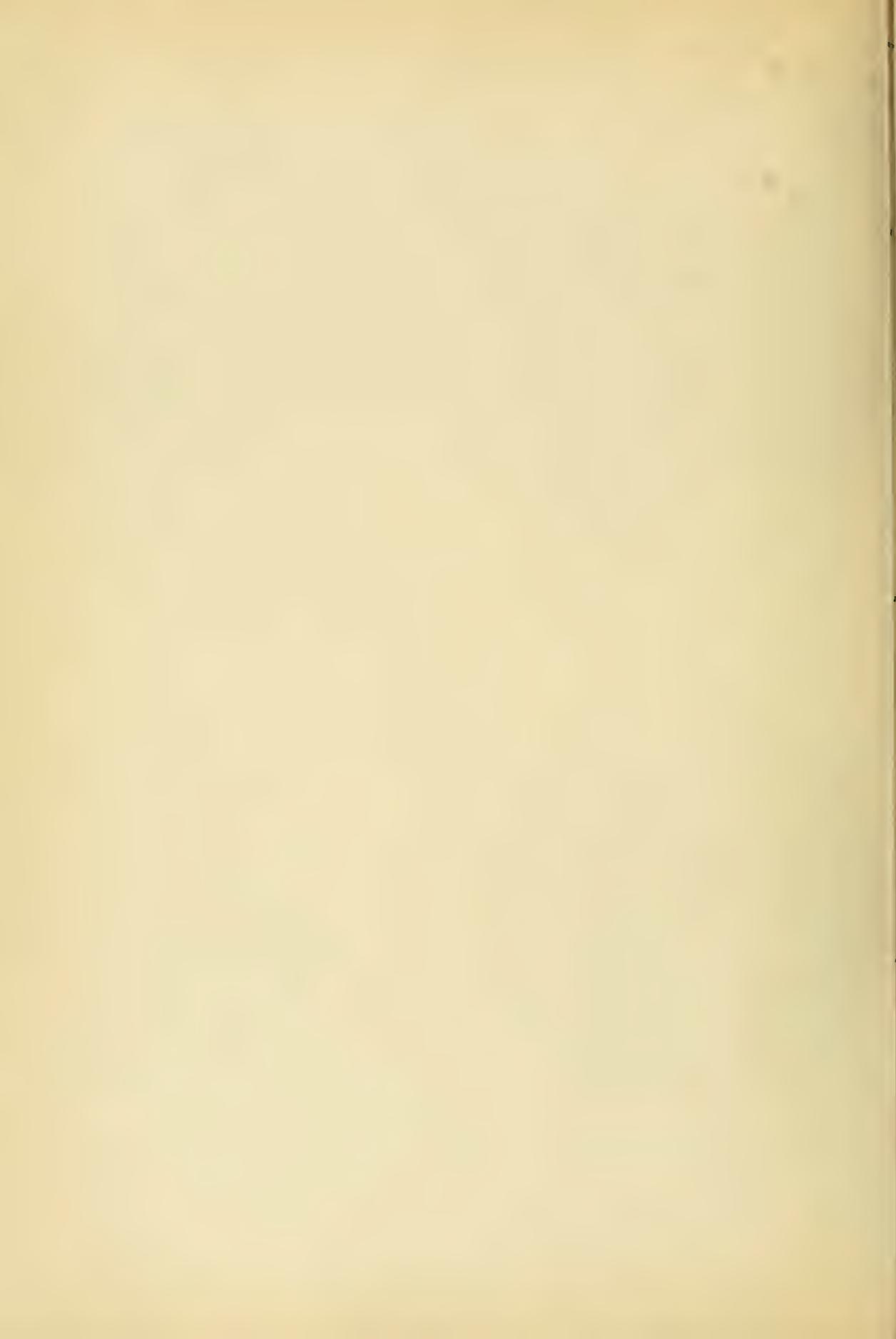


Fig. 4.

*Turmaline*; plate perpendicular to the  $c$ -axis.  
 $d = 1.1$  m.M.;  $A = 44$  m.M.



A NEW PHENOMENON, ACCOMPANYING THE DIFFRACTION OF RÖNTGEN-RAYS  
IN BIREFRINGENT CRYSTALS.



Fig. 5.

*Dextrogyratory Sodium-Ammonium Tartrate (4 H<sub>2</sub>O).*  
Plate perpendicular to the *a*-axis.



Fig. 6.

*Dextrogyratory Sodium-Ammonium Tartrate (4 H<sub>2</sub>O).*  
Plate perpendicular to the *b*-axis.

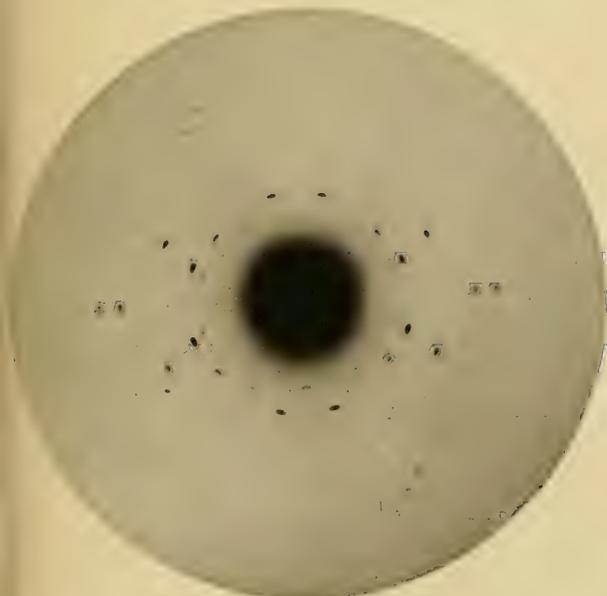


Fig. 7.

*Hambergite*; plate perpendicular to the *a*-axis.  
 $d = 1.56$  m.M.;  $A = 50$  m.M.

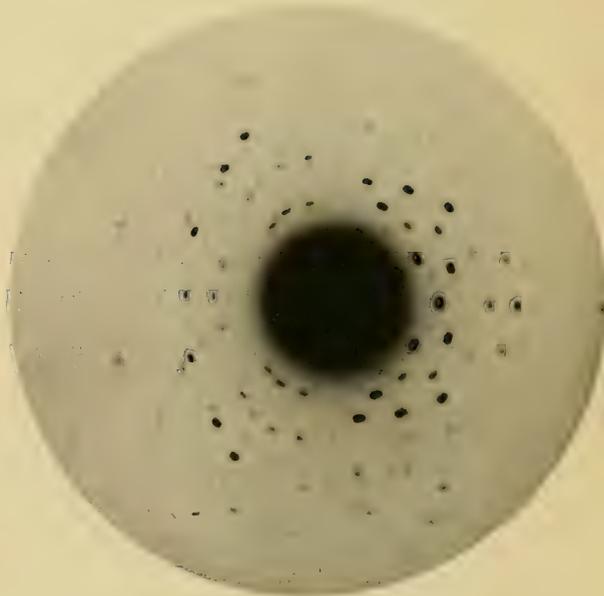
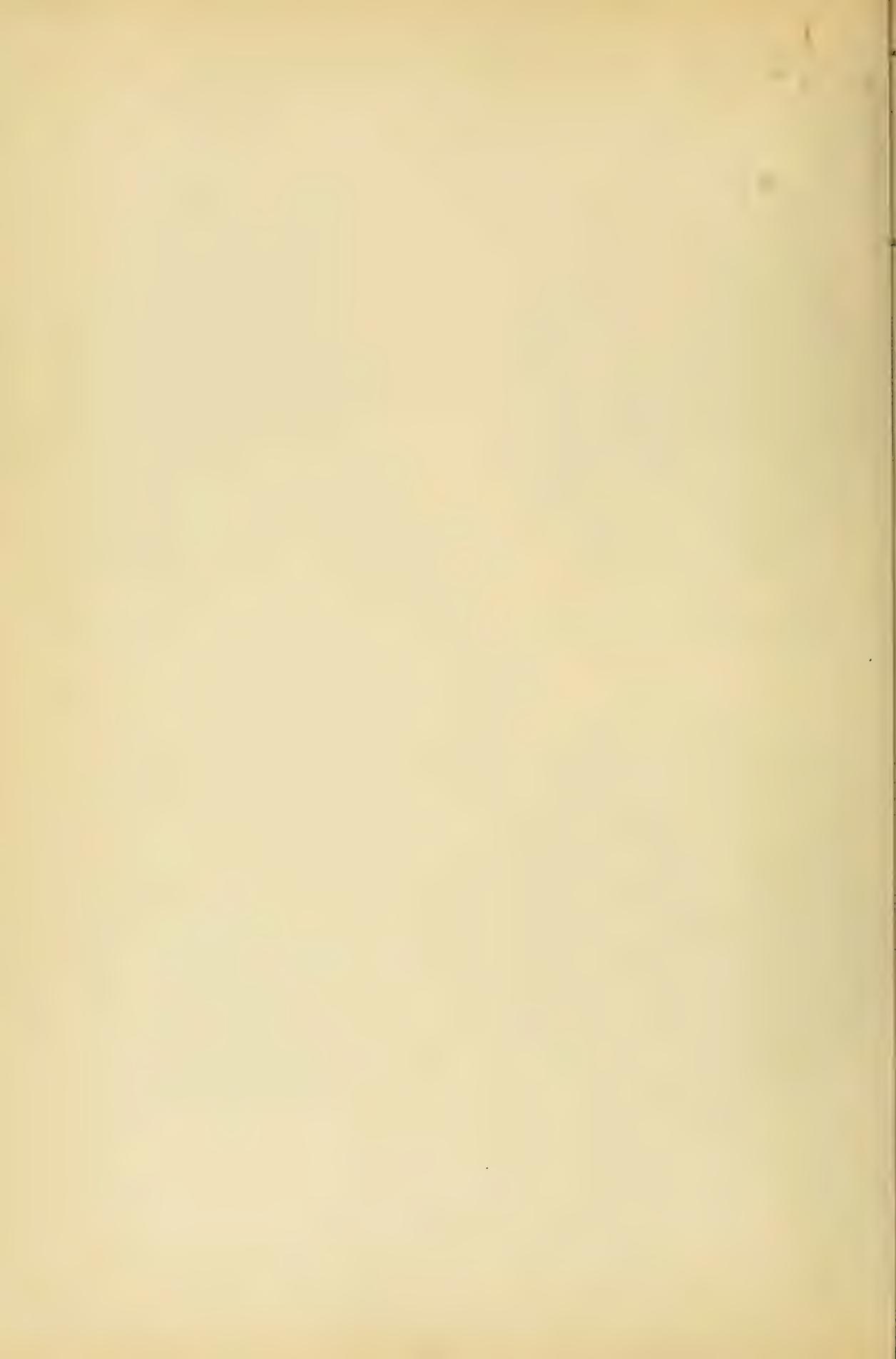


Fig. 8.

*Hambergite*; plate perpendicular to the *b*-axis.  
 $d = 1.54$  m.M.;  $A = 50$  m.M.



A NEW PHENOMENON, ACCOMPANYING THE DIFFRACTION OF RÖNTGEN-RAYS  
IN BIREFRINGENT CRYSTALS.



Fig. 9.  
*Hambergite*; plate perpendicular to the  $c$ -axis.  
 $d = 1.52$  m.M.;  $A = 50$  m.M.

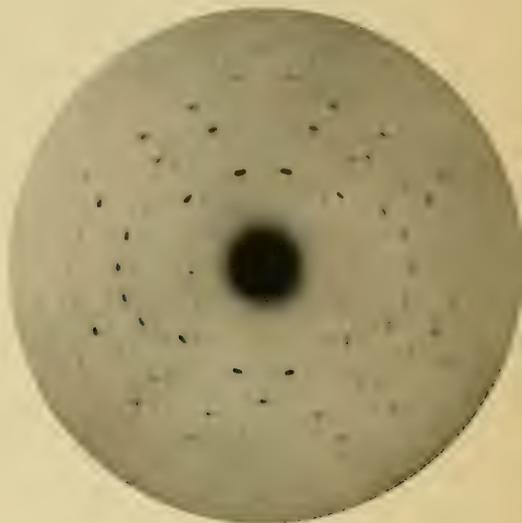


Fig. 10.  
*Benitoite*; plate parallel to  $\{10\bar{1}0\}$   
 $d = 1.52$  m.M.;  $A = 50$  m.M.



Fig. 11.  
*Benitoite*; plate parallel to  $\{\bar{1}2\bar{1}0\}$   
 $d = 1.50$  m.M.;  $A = 50$  m.M.

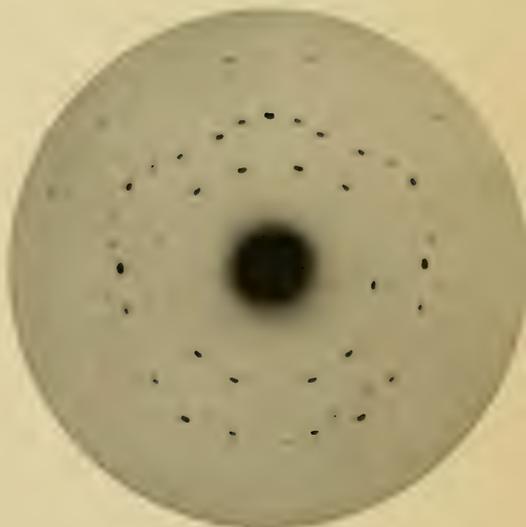
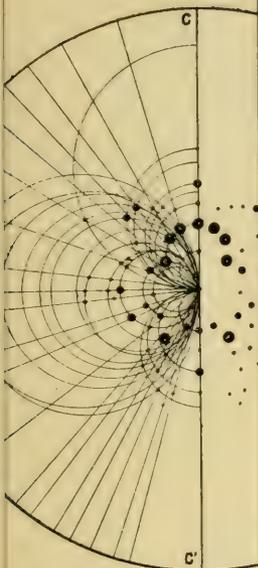


Fig. 12.  
*Benitoite*; plate parallel to  $\{0001\}$   
 $d = 1.50$  m.M.;  $A = 50$  m.M.





6. Stereographical Projection of the Röntgen-pattern of dextrogyronium-Tartrate. Plate

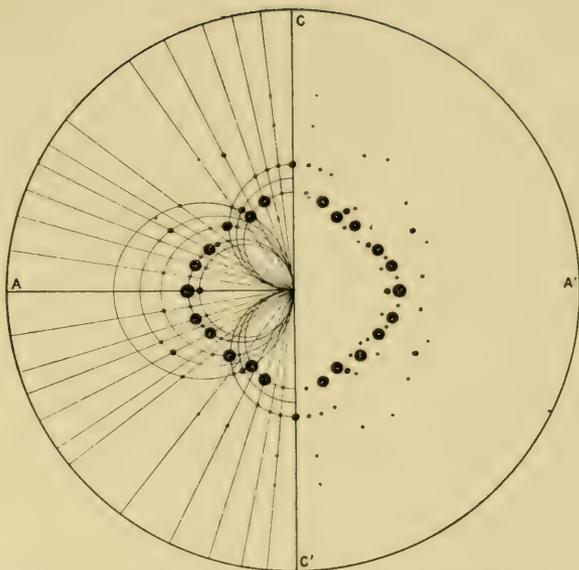
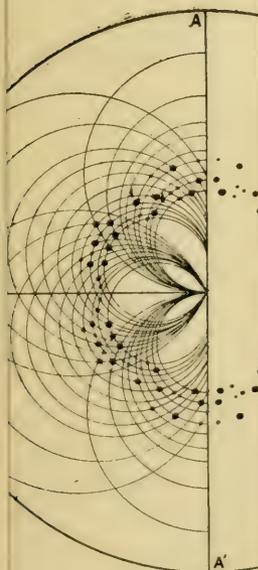


Fig. 13. Stereographical Projection of the Röntgen-pattern of *Benitoite*. Plate parallel to  $(\bar{1}210)$ .



8. Stereographical Projection of the Röntgen-pattern of dextrogyronium-Tartrate. Plate

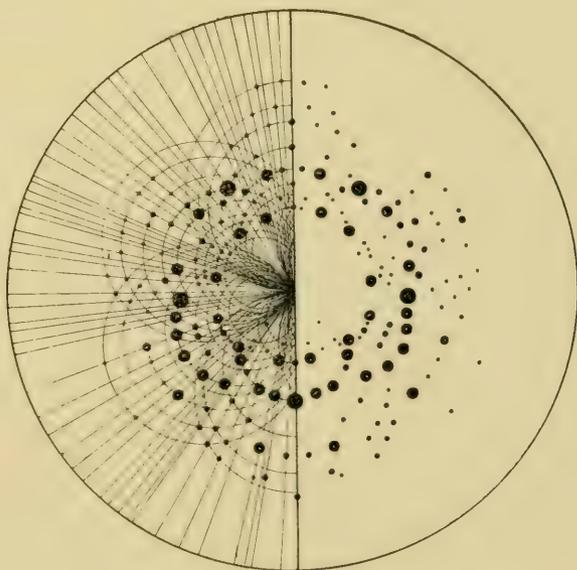


Fig. 14. Stereographical Projection of the Röntgen-pattern of *Benitoite*. Plate perpendicular to the  $c$ -axis.



Fig. 1. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (111).

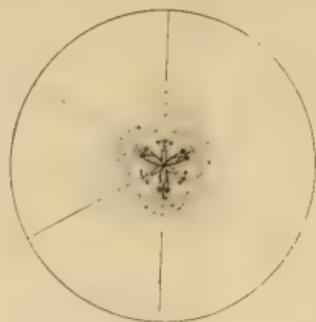


Fig. 2. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (111).

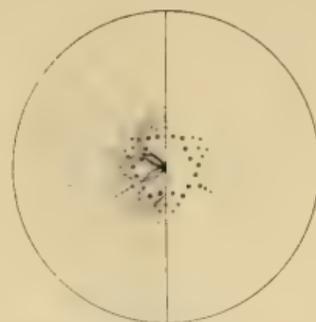


Fig. 5. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (001).



Fig. 6. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (100).



Fig. 9. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (100).

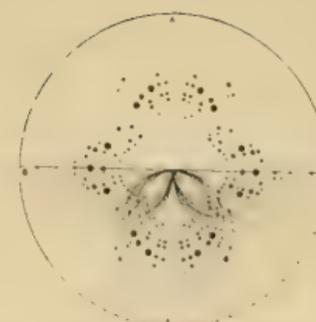


Fig. 10. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (100).



Fig. 11. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (120).

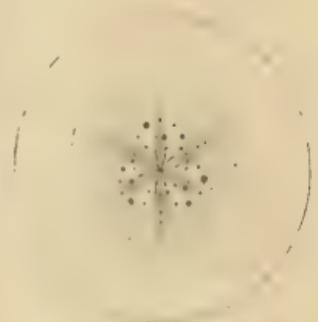


Fig. 3. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (111).

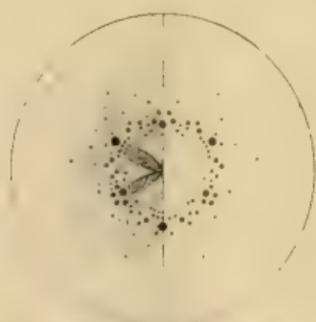


Fig. 4. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate perpendicular to the c-axis.

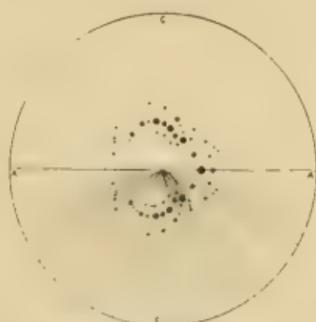


Fig. 7. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (100).

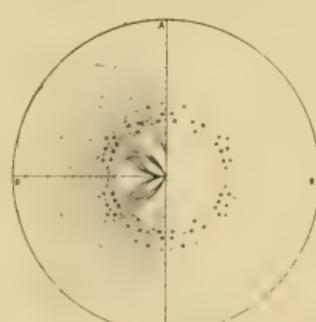


Fig. 8. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (001).

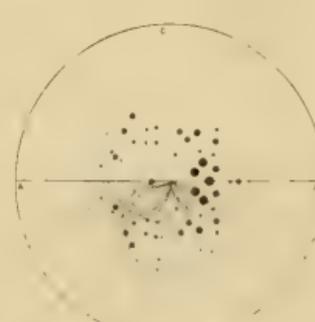


Fig. 11. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate perpendicular to the c-axis.

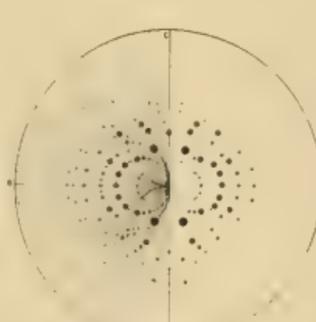


Fig. 12. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (100).

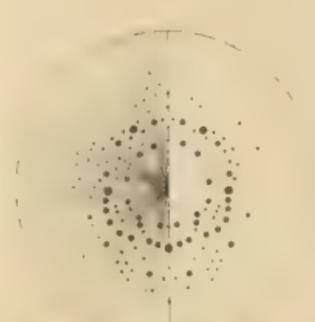


Fig. 14. Stereographical Projection of the Röntgen pattern of diastereoisomeric Tartaric Acid. Plate parallel to (100).

*benitoite*; it appears to be composed of lamellae, which with respect to each other are turned through an angle of  $120^\circ$ , and seem to possess rhombic-hemimorphic or monoclinic symmetry.

The plates parallel to  $\{10\bar{1}0\}$  and  $\{\bar{1}2\bar{1}0\}$  also betrayed this lamellar structure in a more or less convincing way: the plate parallel to  $\{\bar{1}2\bar{1}0\}$  showed this lamellar character very clearly, and was composed of two sets of nearly perpendicular crossing lamellae, which made about  $53^\circ$  with the  $c$ -axis, while an irregular partition in fields of different colour and dichroism could be observed in some cases besides.

The crystals are very strongly dichroitic: for vibrations parallel to the  $c$ -axis the crystals have a deep blue colour, for such perpendicular to the  $c$ -axis, they are almost colourless, with a very faint lilac hue.

The cleavage is very imperfect, and parallel to  $\{10\bar{1}1\}$ ; from the goniometrical measurements it follows, that the pseudo-trigonal complex has an axial ratio of:  $a : c = 1 : 0.7319$ .

In figures 12, 13, 14, are reproduced the stereographical projections of the very fine RÖNTGENograms which were obtained in our experiments. Figures 9, 10, and 11 on plate III are reproductions of the original photographs.

The plate perpendicular to the  $c$ -axis (fig. 14) gave a RÖNTGEN-pattern, which possessed no more than one single plane of symmetry, parallel to  $\{10\bar{1}0\}$  notwithstanding its undeniable trigonal design.

In agreement with this, the image in fig. 13, obtained with a plate perpendicular to  $\{\bar{1}2\bar{1}0\}$ , shows a vertical symmetry-plane. It may appear doubtful whether this image also possesses a horizontal plane of symmetry: a very slight but noticeable difference in the intensity of the spots at the ends of the vertical axis seems to be present.

The question is however, whether this would indicate a real, and in that case very feeble polarity of the  $c$ -axis, or if it should be considered as a photographic effect, caused perhaps by a slight deviation of the plate from its normal position. In fig. 12, obtained by transmission of the pencil of RÖNTGENrays in a direction perpendicular to  $\{10\bar{1}0\}$ , the polarity of the  $c$ -axis is however very much more easily recognisable, — not only in the differences in intensity, but also in the different arrangement of the spots.

However, whether one considers the  $c$ -axis a polar one or not, the combination of the symmetry-properties observed is here geometrically quite impossible also; for if the  $c$ -axis is of a polar nature,

then fig. 14 must be symmetrical with respect to both perpendicular planes; and if the  $c$ -axis is not of that kind, fig. 14 should necessarily possess the same symmetry.

In every case therefore, one plane of symmetry must have disappeared in fig. 14; here also no other supposition is possible than that there must be some reason why the expected spots in directions parallel to the intersection  $(0001) : (10\bar{1}0)$  are completely or partially suppressed. The real symmetry of the pseudotrigonal complex of lamellae can thus be regarded after this as a matter of secondary importance; for it is very well possible, that in fig. 12 also a second symmetry-plane, parallel to  $\{001\}$  has disappeared, and in that case the resulting combination of symmetry-properties would be geometrically impossible too, just as in all preceding cases.

§ 8. We here thus meet the extremely remarkable phenomenon, that in biaxial crystals, in striking contradiction to the experience hitherto gathered from optical isotropous or uniaxial crystals if studied perpendicular to their optical axis, certain symmetry-elements of the RÖNTGENograms which were to be expected according to the LAUE-BRAGG-theory absolutely vanish. Thereby a complex of symmetry-properties is revealed in the complete set of RÖNTGENpatterns of the same crystal, which is geometrically impossible, and which therefore cannot be a representation of the special symmetry of the crystal itself.

As far as experience now goes, and provided that the more complicated case of the mimetic *benitoite* is for the present left out of consideration, the suppression of the spots occurred in two of the cases studied, in those images which are obtained by the transmission of the RÖNTGEN-rays parallel to the optical normal; i.e. the spots disappeared there in the plane in which the differences of the optical elasticity of the crystal are *as great as possible*. In the case of the *sodiumammoniumtartrate* the suppression occurred for crystal-plates either parallel to the optical axial plane, or perpendicular to the second bisectrix; i.e. in the directions of the *greatest* and *smallest* elasticity, not however in the direction of the optical normal.

One would be inclined to explain these phenomena, — just because they are observable exclusively in those crystals whose optical anisotropy is manifested in *all* directions, — by supposing some condition of polarisation of the generated secondary waves, which polarisation would finally find its expression, — somewhat in the same way as in the case of ordinary light-waves, — in an unequivalence of perpendicular directions. Or one again would be inclined to suppose an anisotropy in the mode of motion of the particles

affected by the impulse of the incident rays, in three perpendicular directions, and to investigate the consequences of such a supposition for the process of the generating of the spots on the photographic plate<sup>1)</sup>.

In connection with this last supposition, the question could then be considered once more, whether the unequal deviations of the law of FRANTZ and WIEDEMANN in the principal directions of crystallised bismuth and hematite formerly observed,<sup>2)</sup> were not perhaps to be explained in some analogous way?

But let be it as it may, a final explanation of the phenomena observed here cannot be given at this moment. In any case it has become quite evident, that in the temporarily adopted theory for the diffraction-phenomena of RÖNTGEN-rays in crystals, a certain factor is yet missing, which has the result that the consequences of the theory are in agreement with the experimental results only if it is applied to isotropous crystals or to those in which the transmission of the RÖNTGEN-rays takes place in a direction, in which the crystal behaves like an optically isotropous one.

Only in the last-mentioned cases do the facts appear as full illustrations of the theoretical deductions.

But as long as that theory is unable to explain *why* the facts observed with biaxial crystals do *not* coincide with those expected by it, the theory can hardly be said to give a final explanation of the diffraction-phenomena in crystals at all.

Systematical experiments with the purpose to elucidate these phenomena as well as possible, are momentarily going on.

Groningen, *Laboratories for Physics and for Inorganic  
Chemistry of the University.*  
March 15, 1915.

**Chemistry.** — “*Researches on PASTEUR’S Principle of the Connection between Molecular and Physical Dissymmetry.*” I. By Prof.

Dr. F. M. JAEGER. (Communicated by Prof. VAN ROMBURGH).

(Communicated in the meeting of March 27, 1915).

§ 1. It is now matter of common knowledge among scientists how the classic investigations<sup>3)</sup> of L. PASTEUR, regarding the connection between the so-called “molecular dissymmetry” of organic compounds and their optical behaviour, and especially those investi-

<sup>1)</sup> The case of the *tartrate* has in so far some analogy with that of *cordierite*, that in this case also the optical elasticities in the directions of both the *a*- and *b*-axes, do not differ very appreciably, in comparison with that in the *c*-axis.

<sup>2)</sup> F. M. JAEGER, These Proc. **15**. 27, 89. (1907).

<sup>3)</sup> L. PASTEUR, Recherches sur la Dissymétrie Moléculaire; Leçons professées devant la Société Chimique de Paris, (1860).

gations which bear upon the properties of the racemic and tartaric acids and their salts, — have led to that more detailed conception of the spacial arrangement of the atoms in the molecules, which has finally obtained expression in the stereochemical views of modern times. The conclusion to which PASTEUR was led can be shortly expressed in this way: in all cases where a substance is characterised by a dissymmetrical arrangement of the composing atoms in its molecules, the possibility can be foreseen of the existence of two modifications of that substance, whose physical properties can be described by spacial systems of vectors, which are in the relation to each other of right- and lefthand-systems.

This statement has proved to be satisfactorily general and so indefinite as to have led to numerous remarks and even to misunderstanding. With respect to the second part of the above-mentioned conclusion, there can hardly be any divergence of opinion: it is of course quite apparent, that here only can be question about *vectorial*, never about *scalar* quantities. Thermical, caloric, and volumetrical constants, e.g., will thus be identical with the two modifications in all cases; and from those properties which are expressed by means of vectors, only such can be taken into account, whose descriptive vector-systems will *not* coincide with its mirror-images; the pyro- and piezo-electrical phenomena, etc., which cannot be described by centrally-symmetrical, but only by "polar" vectors.

The first part of PASTEUR's conclusion however will immediately lead to the question: what is the proper meaning of the expression "molecular dissymmetry", and under which circumstances will it manifest itself? It becomes clear on fuller examination, that the introduction of the word "dissymmetry" in these cases, has often caused misconceptions, and that it has led to erroneous or at least incomplete statements, even with well-known authors; and what is more, it seems continually to lead to unintelligibility about the conditions which will determine the isomerism indicated, notwithstanding the evident feeling of incertitude, which can occasionally be stated <sup>1)</sup>.

The doctrine of the so-called "unsymmetric atoms" of LE BEL and VAN 'T HOFF brought, as is well-known, a first rational explanation of that "molecular dissymmetry". Since then the presence of an *n*-valent atom, saturated by *n* unequal substitutes, has begun to be considered as *the necessary condition* which must be fulfilled, if the case of a possible isomerism as foreseen by PASTEUR, is to be realized;

<sup>1)</sup> Conf. CH. M. VAN DEVENTER, Chem. Weekblad **10**. 1046. (1913).

and as GUYE's suggestive ideas prove, they even tried to point out an immediate connection between the more or less considerable degree of such molecular dissymmetry, and the more or less palpable differences, e. g. in *mass*, which can be stated between those  $n$  unequal atoms or radicals<sup>1)</sup>. In that case the idea is evidently always present, that a chemical molecule possessing such "unsymmetric atoms", will necessarily be characterized by a complete *lack of symmetry*, and thus can be defined in the full sense of the word, as an "unsymmetric" molecule.

As long as one is of opinion, that in this question the ordinary *chemical differences* of the radicals which are linked to the multivalent atom, will really be the predominant factor, it perhaps is allowable to consider such a molecule as a spacial complex which does not possess any more symmetry-properties. But it must immediately be pointed out here, that this conclusion is by no means an inevitable one: it must be considered to be quite precipitate, to suppose the molecules of this kind as necessarily unsymmetrical ones for all kinds of physical properties, just because we do not know the undoubtedly very complicated structure of the atoms themselves. The more, as the "absence of symmetry-planes", commonly brought to the fore on this occasion, will by no means involve the absence of any symmetry in such a spacial system, nor will this single condition be sufficient to make the presence of two modifications, which relate to each other as mirror-images, a necessary consequence.<sup>2)</sup>

In connection with these erroneous conceptions about the conditions which will involve the mirror-image-isomerism in the case of such spacial systems, it must be esteemed of the highest importance that we have begun to understand that the presence of an "unsymmetric" multivalent atom, as defined by the conception of LEBEL and VAN

<sup>1)</sup> PH. A. GUYE. Compt. rend. **110**. 744 (1890); Thèse Paris, (1891).

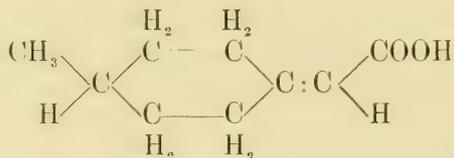
<sup>2)</sup> If for instance one accepts the idea that the atoms of the chemical elements, notwithstanding their different nature, contain some structure-elements which are common to all of them, and that it will principally depend just on the spacial arrangement of those common constituents (e.g. systems of electrons), which will determine the symmetry of the physical properties or at least of some of them in the resulting substances, — then it does by no means follow from the chemical inequality of the substitutes in the molecule, that the spacial system of those determining structure-elements of the atoms, necessarily represents a *non-symmetrical* complex. As long as we do not know, on what particular circumstances the physical dissymmetry of the molecules properly depends, it is not allowable in my opinion to consider the chemical inequality of the substitutes as the *necessary* condition of the physical dissymmetry of the substance; it can at best be esteemed a *very favourable moment* for it.

'T HOFF, must really be considered only as a very favourable factor with respect to the mentioned possibility of such isomerism; but that the chemical difference of the substitutes in this case may not absolutely be regarded as the predominant factor therein.

Finally the right- and left-hand isomerism must appear possible in all those cases, where, — it matters not whether the substitutes are equal or unequal, — the spacial arrangement in the molecule and the distribution of the intramolecular forces, will fulfil the special conditions of symmetry which can be generally deduced and formulated for all kinds of spacial systems differing from their mirror-images.

§ 2. The investigations of the last few years have completely justified the conclusion, that in the first instance it depends in this question upon the spacial arrangement *alone*. That e.g. the differences of *mass* of the substitutes, are no measure for the lower or higher degree of "molecular dissymmetry", has inter alia resulted from FISCHER'S experiments<sup>1)</sup> relating to the *propyl-isopropyl-cyano-acetic acid*, whose optically active components show a fairly high specific rotation (about  $11^\circ$ ), notwithstanding the *equal masses* of both the hydrocarbon-radicals in their molecules. Furthermore SWARTS tried to prove firstly that no other carbon-atoms need to be linked directly to the unsymmetric atom in such active molecules; but it was only recently proved in a final way by POPE, in the case of the *Ammonium-salt of Chloro-jodo-methane-sulfonic acid*<sup>2)</sup>.

And that also the above-mentioned isomerism can occur in cases where no symmetrical atoms, surrounded by unequal substituents, are present, was proved some years ago by the experiments of POPE, PERKIN and WALLACH<sup>3)</sup>, with respect to the *1-methyl-cyclohexylidene-4-acetic acid*:



However the solubility<sup>4)</sup> of these and related substances in almost

<sup>1)</sup> E. FISCHER and E. FLATAU. Ber. d. d. Chem. Ges. **42**. 981 (1909).

<sup>2)</sup> W. J. POPE and J. READ. Proceed. Cambridge Phil. Soc. **17** (1914); Trans. Chem. Soc. **105**. 811 (1914).

<sup>3)</sup> POPE, PERKIN and WALLACH. Trans. Chem. Soc. **95**, 1789. (1909); POPE and PERKIN, *ibid.* **99**. 1510 (1910).

<sup>4)</sup> According to a private communication given by Prof. POPE to me.

all solvents is so great, that it was hitherto impossible to prove the correctness of PASTEUR'S principle in these cases, just with respect to the crystalforms of the antipodes.

The strongest evidence however in favour of the views previously explained about the necessary conditions for the occurrence of mirror-image-isomerism, can be deduced from the theoretically comparatively simple cases which for the first time became known as a result of A. WERNER'S masterly investigations on the complex-salts, and more especially of the *luteo-triaethylenediamine-cobaltic salts*<sup>1</sup>).

Later on he found analogous phenomena with a number of other salts with complex ions, e.g. with the analogous derivatives of oxalic acid. Not only did these facts prove the correctness of WERNER'S views considering the *spacial* arrangement of the six coordinated substitutes round the polyvalent central-atom, but they have also brought direct proof of the correctness of the other idea, that in the question of "molecular dissymmetry", as commonly understood, it is *not primarily* the inequality of the substituents, but exclusively *their spacial arrangement*, which is of importance.

A new problem is thereby brought to the fore: to find the circumstances and conditions, which will cause a spacial configuration of the atoms in the molecules, which will be different from its mirror-image even in those cases where no chemical differences between those substitutes are present<sup>2</sup>).

<sup>1</sup>) A. WERNER. Ber. d.d. Chem. Ges. **45**. 121. (1912); **47**. 1960, 3093. (1914).

<sup>2</sup>) In this connection it may be well, shortly to remind of the conditions for the occurrence of spacial configurations, which will not be congruent with their mirror-images, and to mention the significance there-with of the commonly emphasized "lack of symmetry-planes" in this phenomenon. If one chooses as the descriptive "symmetry-elements" for such spacial arrangements: the *symmetry-axes*

(period =  $\frac{2\pi}{n}$ ) of the *first* and of the *second* class ("axes of alternating symmetry"),

— then one can say that all configurations which do *not* possess such axes of the second class, will be different from their mirror-images. All such configurations, which differ from their mirror-images, can possess only *axial* symmetry. As an axis of the second class, for which  $n = 2$ , corresponds to a "centre of symmetry", and one for which  $n = 1$ , corresponds to a mere mirror-plane, it becomes clear that such "enantiomorphic" arrangements neither possess a centre of symmetry, nor a plane of symmetry. *But the reverse statement is not true*: among the 32 possible symmetrical groups of crystallography e.g. there are already *three* which do *not* possess any plane of symmetry, and whose configurations, notwithstanding that, do *not* differ from their mirror-images (in the cases apparently, where there is only one axis of the second class present, with  $n = 2, 4$  or  $6$ ). And there are several groups, which have *no* centre of symmetry, and are however identical with their mirror images. It can moreover be remarked here, that axes of the

§ 3. Evidently it must be considered of the highest importance to bring in this theoretically simplest case, — that namely where by the equality of the substitutes the “molecular dissymmetry” manifests itself only by the spacial arrangement of equal things, — the complete proof, that PASTEUR’s principle is really right. It is therefore necessary to prove not only the optical activity of the antipodes obtained, but at the same time the crystallographical *enantiomorphism* of them. It was with this purpose, that the following investigations were made, and especially, because there are known cases, in which notwithstanding the clearly stated optical activity, an enantiomorphism of the antipodes could *not* be proved with certainty, as e.g. in the case of *lupeol*<sup>1)</sup>.

According to WERNER the enantiomorphism of these isomerides has been hitherto proved only in one single case: i.e. with the *potassium-salt* of the *rhodiumoxalic acid*:  $\{Rho(C_2O_4)_2\} K_3 + 1 H_2O$ . These crystals however being, according to that author, *triclinic*, they must then evidently belong to the *pedial* class of that system, where *no* symmetry at all is present. It is moreover well-known, that a number of substances in this class without any trace of optical activity, also crystallise; I myself described a very convincing instance of this kind some time ago with the *inactive diethylenediamine-diisorhodanato-*

*chromichloride*: <sup>2)</sup>  $\left\{ Cr \begin{matrix} (Aein)_2 \\ (NCS)_2 \end{matrix} \right\} Cl$ , a substance which on account of its stereochemical configuration must undoubtedly be considered as a *racemic* compound of two enantiomorphic modifications. The occurrence of this triclinic-pedial symmetry is therefore no a very favourable circumstance for the convincing proof of the here discussed connection; and it thus seemed necessary to give the desired crystallogonomical proof in less doubtful cases and with substances showing a higher crystallographical symmetry. In what follows it will become clear, what has been the result of it.

It may be again mentioned here, — before giving the detailed description of our objects in the next publication, — that WERNER moreover succeeded recently in proving, that for the occurrence of the mirror-image-isomerism, the presence of *carbon-atoms* in the molecule evidently is as little a necessary condition, as that of *unsymmetric atoms* in general. He was able to obtain the antipodes of the

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second class, whose number *n* is divisible by 4, can never be replaced by any combination of axes of the first class with a centre of symmetry, or with a plane of symmetry.

<sup>1)</sup> F. M. JAEGER. Zeits. f. Kryst. **44**. 568. (1908).

<sup>2)</sup> F. M. JAEGER. Zeits. f. Kryst. **39**. 579. (1904).

*dodecamine-hexol-tetra-cobaltibromide*<sup>1)</sup>, which salt has the same type as the triethylenediamine-cobalti-salts, but no longer possesses one single carbon-atom.

§ 4. As suitable objects for this investigation I have chosen the *luteo-triethylenediamine-cobalti-salts* of the type:  $\{Co(Aein)_3\} X_3$ , in which  $X$  was varied in several ways, for the purpose of elucidating as well as possible the mere influence of the complex cation. I prepared these salts, starting from the already obtained optically active components of the corresponding *bromide*, and by making them react in aqueous solution with the silversalts of nitric acid, chloric acid, perchloric acid, etc., or by double decomposition with the potassium-, or sodiumsalts of hydrojodic or rhodanic acid. The optically active bromides themselves were obtained from the racemic salt by means of the corresponding *bromotartrates*, whose dextrogyratory form is also described in the next paper. The great stability of the active components, even when heated in aqueous solution, was of preponderant importance in these experiments; an autoracemisation does not occur in any appreciable degree.

The racemic salt was prepared by two different methods: 1. by starting from *praseo-diethylenediamine-dichloro-cobalti-chloride*:  $\left\{ Co \begin{matrix} (Aein)_2 \\ Cl_2 \end{matrix} \right\} Cl$ , and heating with a 10 %-solution of ethylenediamine; and 2. by starting from *purpureo-pentamine-chloro-cobaltichloride*:  $\left\{ Co \begin{matrix} (NH_3)_5 \\ Cl \end{matrix} \right\} Cl_2$ , and transforming it by boiling it, for a longer time with ethylenediamine. This last method of preparation, described by PFEIFFER<sup>2)</sup>, was also followed, because the description of the obtained salt by this author differs in some particulars from that, given with respect to the salt obtained in the first mentioned method. However by a more detailed comparison of the two products it was clearly pointed out, that notwithstanding slight differences in the external habitus of the racemic salt in the two cases, the optically active products were perfectly identical; and that the preparations obtained by the two methods, must undoubtedly be considered as quite the same. (Vid. publication II).

With respect to the isomerism i.e., this can in all cases be illustrated for the complex cation by means of the following perspective drawings, (fig. 1), which can be constructed immediately, starting

<sup>1)</sup> A. WERNER. loco cit., 3093 (1914).

<sup>2)</sup> PFEIFFER, Ann. der Chem. **346**, 59, (1906).

from WERNER's well-known octahedral arrangement of the six equivalent coordination-places round the central cobalt-atom.

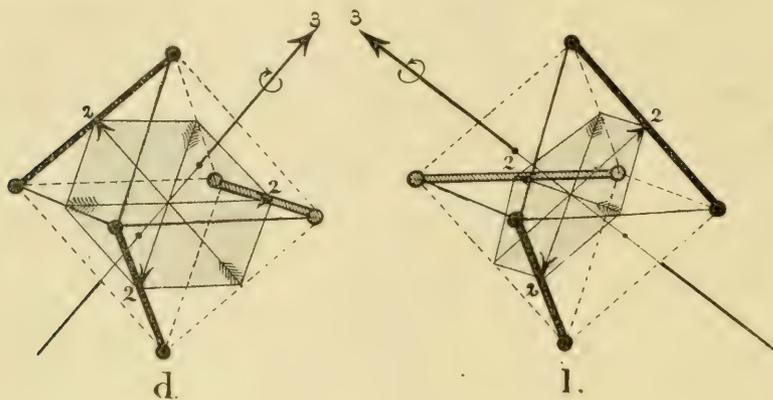
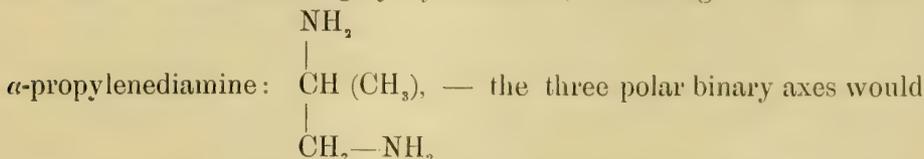


Fig. 1.

A more detailed study of the real symmetry of these spacial arrangements, in connection with the perfectly symmetrical atomistic configuration of the ethylenediamine-molecule itself, shows how these complex cations are rather highly "symmetrical"; they possess the following symmetry-elements: one bipolar ternary principal axis, and three polar binary axes in a plane perpendicular to the ternary axis, intersecting each other at angles of  $60^\circ$  (or  $120^\circ$ ). In fig. 1 the plane of these three polar axes is drawn parallel to the face of the octahedron, lying in the octant *right- and left-above*. There is no symmetry-centre nor any symmetry-plane present in the configuration. The symmetry deduced is the same as in crystallography is described as characteristic of the forms of the *trigonal-trapezohedrical* class, which symmetry is shown also e.g. by the crystals of *cinnabar*, *quartz* and some *camphora*-species, etc. Just as in the case of these substances, both the cations here schematically drawn are *not* identical with their mirror-images, and it is for this reason, that the salts derived occasionally occur in two modifications, which are to each other in the relation of right- and left-handed forms. It may be remarked that a slight indication of the trigonal symmetry of these cations may be observed in the fact, that under the racemic compounds the *chloride* and *bromide*, crystallising with *three* water-molecules, and also the racemic *nitrite*, possess an apparent or real *trigonal* symmetry (vid. paper II). However the corresponding antipodes of the *bromide* unhappily crystallise with *two* molecules of water, while the tetragonal or rhombic symmetry of these optically active salts, which occurs in several cases, can more-

over not be easily brought into immediate connection with the supposition of the presence of a ternary axis in the molecules. The trigonal symmetry of the racemic bromide moreover will appear to be only an *apparent* one: these crystals are really only lamellar intergrowths of probably monoclinic symmetry.

Furthermore it may be remarked here, that if the three equal substitutes were *not* highly symmetrical, — as e.g. in the case of



in fact disappear in the cations, even if the three molecules of the base were placed in an analogous way, but that the ternary axis, — these being of a polar nature, — would be preserved in salts of the type:  $\{Co (\text{Propin})_3\} X_3$ . However it is by no means impossible in this case, that one of the three substitutes was present in an antilogous (reversed) position with respect to the other two; in that case the cation would no longer possess any symmetry-element whatever, and the possibility could then be foreseen, that two more mirror-image-isomerides might on occasion occur again. Thus, if one excludes for the present the possibility of a separation of the  $\alpha$ -propylenediamine itself into two antipodes, even then for salts of the type  $\{Co (\text{Propin})_3\} X_3$  a greater number of isomerides might be expected. It is not at all impossible, that the difficulties, which always in our experience present themselves, if one tries to get the salts of this type in well developed crystals, must be connected with the fact that really here a *mixture* of isomeric salts is always operated with, which of course will not crystallise as well as in the case of a single, chemically homogeneous compound. We hope in the future to have an opportunity, of again drawing attention to the properties of these salts.

§ 5. The crystallographical material, collected during these investigations will be published in the next paper (II). The data however with regard to the *rotation* of the salts studied in solution, and of their remarkable *rotation-dispersion*, may find their place here, as they can give the right impression about the fact, that one has in these cases in reality to deal with “dissymmetric” compounds, as understood in PASTEUR’S principle and to what high degree.

These experiments were made with a large LIPPICH-polarimeter from SCHMIDT and HAENTSCH; it possessed a telescope-field with three

divisions, and it was combined with a spectral monochromator. By comparison with the spectra of hydrogen and of the metals: sodium, lithium, calcium and thallium, the micrometerscrew of the monochromator was calibrated beforehand. As luminous source a NERNST-lamp was used; the tubes had in all experiments a length of 20 cm.

The wave-lengths are expressed in ÅNGSTROM-units (A. U.); the molar rotation  $[m]$  was calculated from the expression:

$$[m] = \alpha \frac{V}{l};$$

in which  $\alpha$  is the observed rotation,  $l$  the length of the tube in cm., and  $V$  is the volume of the solution in cm.<sup>3</sup>, containing just one grammolecule of the anhydrous salt. With the purpose of avoiding too big numbers especially in the graphical representation (fig. 2),  $[m] \cdot 10^{-1}$  is everywhere given.

The exact determination of the rotation-dispersion was in all cases limited by the strong absorption of the redbrown or yellow solutions; for the same reason too concentrated solutions could not be studied.

The exactness of these determinations is of course not unappreciably less than in the case of colourless solutions; however a schematic and fairly true expression of the dispersion was beyond doubt obtained in this way.

It was observed moreover, how in the immediate neighbourhood of an absorptionline, the rotation reaches a maximum value, and then decreases very rapidly, in some cases the algebraic sign of the rotation being even reversed. Probably the remarkable phenomena of abnormal rotation-dispersion, observed by WERNER in some cases, among others with the trioxalo-derivatives, etc., will prove to be in an analogous connection with the absorption-lines present in the spectra of the solutions of these salts.

The molecular rotation-dispersion of the *luteo-triethylenediamine-cobalti-cation* has an enormous value: for the sake of comparison the corresponding curve for *saccharose* is reproduced in fig. 2 on the same scale.

The temperature of the studied solutions varied from 15°—20° C.; special experiments at 10°, 18°, 54° and 98° showed us that the rotation does not change very appreciably with the temperature.

The results of the measurements are reproduced in the following tables; all rotations are calculated with respect to one gram-molecule of the *anhydrous* salts.

I. *Dextrogyratory Triethylenediamine-Cobalti-Bromide.*

*Solution A* contained 0.5720 gram of the hydrated salt to 29.89 grams of water; the specific gravity at 15° C. was: 1.010.

*Solution B* contained 2.3669 grams of the hydrated salt in 32.56 grams of water; at 15° C. the specific gravity of the solution was : 1.035.

*Solution C* contained 2.0126 grams of crystallised salt to 31.49 grams of water; the specific weight at 15° C was : 1.026.

With solution *A* the limits of exact determination were given for the wave-lengths: 6900 A.U. and 5420 A.U. respectively; with *B* and *C* observation could only satisfactorily take place for wave-lengths smaller than 5600 A.U.

Wave-length in A. U.	Observed Rotation			Molar Rotation $[\alpha] \times 10^{-1}$		
	<i>A</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>B</i>	<i>C</i>
6750	+ 1.07	—	+ 3.95	+ 145.0	—	+ 164.7
6600	1.37	+ 5.77	5.46	185.7	+ 212.4	227.7
6425	1.95	7.84	7.34	264.3	288.6	306.1
6265	2.67	10.02	9.44	361.9	368.9	393.7
6100	3.29	12.97	12.29	445.9	477.5	512.6
5910	4.37	16.47	15.30	592.3	606.4	638.1
5760	5.59	20.77	19.85	757.7	764.7	827.9
5595	7.89	—		1069.4	—	

II. *Laevogyratory Triethylenediamine-Cobalti-Bromide.*

*Solution A* contained 0.5651 gram of crystallised salt in 25.85 grams of water; the specific gravity at 15° C. was: 1.011.

*Solution B* contained 0.1239 gram of the hydrated salt in 26.03 grams of water.

*Solution C* contained 2.1759 grams of crystallised salt in 30.11 grams of water; the specific gravity of the solution was 1.033 at 15° C.

*Solution A* allowed the passage of the light between ca. 6900 A.U. and 5400 A.U.

*Solution B* between 7000 A.U. and 4850 A.U.; *solution C* between 6900 A.U. and 5700 A.U.

Wave-length in A.U.	Observed Rotation			Molar Rotation $[m] \times 10^{-1}$		
	A	B	C	A	B	C
6750	- 1.06	—	- 4.43	- 126.2	—	163.4
6600	1.82	—	6.36	216.8	—	234.6
6425	2.37	—	8.51	282.3	—	313.9
6265	3.16	—	10.23	376.4	—	377.4
6100	3.97	—	12.91	472.8	—	477.0
5910	5.06	- 1.05	16.62	602.6	- 571.0	613.1
5760	6.60	1.43	21.20	786.1	777.7	782.1
5595	8.81	1.68	—	1049.3	913.6	—
5420	11.95	2.32	—	1423.3	1261.7	—
5260	—	3.25	—	—	1767.4	—
5085	—	4.20	—	—	2284.1	—

Evidently a rational connection between the deviations of these numbers and the degree of dilution of the aqueous solutions, can not be deduced. As *mean* values, used in the construction of the dispersion-curve, we have thus the following numbers:

Wave-length in A. U.	Molar Rotation $[m] \times 10^{-1}$		Mean value:
	Dextrogyratory salt	Laevogyratory salt	
6750	+ 167.2	- 163.4	± 165.3
6600	206.2	225.7	215.9
6425	282.8	298.1	290.4
6265	374.0	376.9	375.4
6100	480.6	474.9	477.8
5910	603.1	595.6	599.3
5760	797.0	782.0	790
5595	1080	981.5	931
5420	1456	1342	1399
5260	2038	1767	1903
5085	2469	2284	2377
4920	2705	—	2705

In the third column the mean values of the numbers of the second column are mentioned; with these numbers the dispersion-curve was drawn.

**III and IV.** *Dextro- and Laevogyratory Triethylenediamine-Cobalti-Nitrate.*

In an analogous way to that of both bromides, the dispersion-curves for the other salts were drawn.

Of the dextrogyratory nitrate a solution was used, containing 0.2085 gram of the salt in 30.21 grams of water; the numbers of the laevogyratory nitrate relate to a solution, containing 0.2534 gram of the salt in 30.52 grams of water. The specific gravity did not differ appreciably from that of pure water.

The determinations were too uncertain for values of  $\lambda$  smaller than 5085 A.U.

Wavelengths in A. U.	Observed Rotation		Molar Rotation: $\times 10^{-1}$		Mean value
	Dextrogyra- tory salt	Laevogyra- tory salt	Dextrogyra- tory salt	Laevogyra- tory salt	
6600	+ 0°44	— 0°62	+ 136°5	— 158°8	$\pm$ 147°7
6425	0.66	0.85	204.7	217.7	211.2
6265	0.92	1.07	285.4	274.0	279.2
6100	1.17	1.43	362.9	366.2	364.5
5910	1.56	1.80	483.9	461.0	472.5
5760	2.10	2.33	651.3	596.8	624.0
5595	2.98	3.18	924.3	814.5	870.0
5420	3.88	4.23	1203.0	1083.0	1143.0
5260	5.36	5.65	1663.0	1447.0	1555.0

**V and VI.** *Dextro- and Laevogyratory Triethylenediamine-Cobalti-Iodide.*

The numbers relate in the case of the dextrogyratory salt to a solution, which contained 0.1775 gram of the crystallised salt (with 1 H<sub>2</sub>O) in 30.01 grams of water; in the case of the laevogyratory salt, the concentration was: 0.1679 gram of salt to 30.20 grams of water.

For wave-lengths greater than 6600 A.U. and smaller than 4920 A.U., almost no light comes through the liquid.

Wave-length in A. U.	Observed Rotation		Molar Rotation: $\times 10^{-1}$		Mean value:
	Dextrogyra- tory salt	Laevogyra- tory salt	Dextrogyra- tory salt	Laevogyra- tory salt	
6600	+ 0°39	—	+ 211°4	—	211°4
6425	0.50	— 0°83	271.1	276°1	273.6
6265	0.67	0.61	363.2	352.1	357.1
6100	0.86	0.82	466.2	473.3	469.7
5910	1.08	1.06	585.5	611.9	598.7
5760	1.45	1.32	786.1	762.0	774.0
5595	1.93	1.90	1046.0	1097.0	1072.0
5420	2.60	2.53	1409.0	1460.0	1435.0
5260	3.40	—	1843.0	—	1843.0
5085	3.98	—	2158.0	—	2158.0

**VII and VIII.** *Dextro- and Laevogyratory Triethylenediamine-Cobalti-Rhodanide.*

The dextrogyratory solution contained 0.2065 gram of the salt in 30.20 grams of water; the laevogyratory in the same way: 0.2455 gram in 30.15 grams of water. For wave-lengths greater than 6600 A.U. and smaller than 5260 A.U., the measurements with the polarimeter were no more reliable.

Wave-length in A. U.	Observed Rotation		Molar Rotation: $\times 10^{-1}$		Mean value:
	Dextrogyra- tory salt	Laevogyra- tory salt	Dextrogyra- tory salt	Laevogyra- tory salt	
6425	+ 0°54	— 0°76	+ 164°3	— 194°4	$\pm$ 179°3
6265	0.81	1.12	246.5	286.6	266.6
6100	1.40	1.47	426.0	376.1	401.1
5910	1.56	1.98	474.7	506.6	490.7
5760	1.80	2.60	547.7	665.2	616.5
5595	2.18	3.55	663.4	908.3	781.3
5420	—	5.20	—	1330.0	1330.0



the passage of light between the wave-lengths 6600 A.U. and 4920 A.U. The numbers for the two components were almost the same within the limits of experimental errors. The foregoing data are those obtained with the laevogyrotory salt: (see p. 1231)

For the sake of comparison the *mean* values of the molar rotations of the different salts are once more reviewed in the following table:

Wave-length in A. U.	Molar Rotation $\times 10^{-1}$				
	Bromides	Iodides	Nitrates	Perchlorates	Rhodianides
6750	165°	—	—	—	—
6600	216	211°	148°	212°	—
6425	290	274	211	327	179°
6265	375	357	279	407	267
6100	478	470	364	444	401
5910	599	599	472	513	491
5760	790	774	624	743	616
5595	931	1072	870	999	781
5420	1399	1435	1143	1407	1330
5260	1903	1843	1555	1804	—
5085	2377	2185	—	2592	—
4920	2705	—	—	—	—

From this table, and from fig. 2, one can see immediately, that in the first place the enormous magnitude of the dispersion and the mean shape of the dispersion-curves manifest themselves in all cases in a quite analogous way; the predominant influence of the complex cation being thus placed beyond doubt. This predominant influence of the spacial configuration of the complex ion in compounds of this kind, was, as I have previously had an opportunity (*Zeits. f. Kryst.* **39**, 575 (1904)) of showing, to a certainty brought to the fore by the fact that all these complex cobalti-salts reveal close crystallo-umical family-relations. The probability for the assumption of an octahedral or pseudo-octahedral arrangement of the six coordination-

places round the central metal-atom, is well illustrated by the fact that not only do most of these salts possess a high crystallographic symmetry (vid. p. 574 of the mentioned paper), but also, that in the case of the optically active components of the *triethylenediamine*-salts studied here, a *rhombic* or *tetragonal* symmetry is everywhere found, with a mean parameter-ratio oscillating between 0,82 and 0,86.

It is however evident at the same time, that the influence of the cation is undoubtedly varied by the presence of different anions:  $Br'$ ,  $J'$ ,  $NO_3'$ ,  $ClO_4'$  and  $CNS'$  in the solutions; and in particular it becomes evident, that the influence of *halogen-*, or *halogen-containing* anions, will differ appreciably from that of the ions  $NO_3'$  and  $CNS'$ . This difference manifests itself very plainly in the *greater* values of  $[m]$  for the same wave-lengths, with salts of the first group, in comparison with those of the second group.

This can most evidently be seen for those wave-lengths, for which the measurements can be made most accurately:

A.U.	Mean value of $[m] \times 10^{-1}$ for the bromides, iodides and perchlorates:	Differences $\angle$	Idem, for the rhodanides and nitrates:	Differences $\Delta$
6265	380°		273°	
		84		109
6100	464		382	
		106		100
5910	570		482	
		189		138
5760	759		620	
		242		211
5595	1001		831	

The question, in how far this different influence is possibly linked directly with a not yet complete electrolytic dissociation in the solutions, could perhaps be answered by the determination of  $[m]$  for infinite great dilutions; however, because of the embarrassing absorption in the coloured solutions, the measurements are not sufficiently accurate to elucidate this matter quite finally.

§ 7. While now by the foregoing investigations the positive and negative optical activity of these complex salts appears to occur beyond all doubt, it must now be our task to investigate the correctness of the second part of PASTEUR'S conclusion also: in how far the results of the crystallographical research is able to demon-

strate an existent connection between this optical activity of these antipodes and their enantiomorphism?

As will be seen in the following, it must now be considered as a very remarkable fact, that the occurrence of enantiomorphic forms with these antipodes, can be stated in a few cases only, while in most of the cases studied not only could no argument be given to make the existence of such enantiomorphism probable, but it could be even demonstrated to be absent, as follows from the certain occurrence of holohedrical forms in these crystals.

We are thus compelled to suppose, — in contradiction to the now still universally accepted doctrine about the necessary connection between the optical activity of crystals and the mere “axial”-symmetrical molecular arrangement of their crystal-structure, — that crystalforms can correspond to such optically active substances, whose symmetry appears to be holohedrical; just as the reverse is the case e.g. with crystals of dextro- and laevogyratory sodium-chlorate, where the enantiomorphic molecular structures are built up by optically *inactive* molecules.

Properly speaking, — of all the salts of this series, only in the cases of the *nitrates* and of the *perchlorates* could it be demonstrated beyond doubt, that a “hémiedrie non superposable” really occurred. In all other cases it was *not* present, or possibly, notwithstanding the enormous optical activity, — so feebly revealed itself, that no rational proof of its existence could be given: on the contrary, in the cases of the *iodides* and *rhodanides* all evidence was certainly present in favour of a true holohedrical symmetry.

Also all experiments, made with the purpose of varying the crystal-habitus by the admixture of other salts in the solutions, in such a way that mere “axial”-symmetrical crystalforms would appear, were without any positive result as far as this problem is concerned.

The crystals of the dextro-, and laevogyratory *bromides* e.g., remained identical under the most varied circumstances: in solutions, containing sodiumbromide for instance, more needle-shaped crystals were obtained, which were however again the same for the two antipodes and evidently represented no other than holohedrical forms.

As far as our experience now goes, it would be only dogmatical, to persevere in the doctrine of the necessary axial-symmetrical nature of the dextro-, and laevogyratory crystals in cases like these, where no argument could be brought in favour of that supposition, while there are many indications just against the occurrence of enantiomorphic forms.

§ 8. If we thus review the facts here mentioned and later-on to be demonstrated in detail, we can consider it as proved that in all the *luteo-triethylenediamine-cobalti-salts*, — just as is foreseen by PASTEUR'S principle, — the spacial configuration in the molecules, different from its mirror-image, is always without exception combined with an enormous optical activity of their solutions; that the enantiomorphism of their crystalforms however may sometimes be revealed, but evidently does *not necessarily* appear. From this fact, one may furthermore conclude, that the optical activity of the molecules principally seems to be determined by the "unsymmetrical" arrangement of the substitutes, as understood by PASTEUR, and that it may reach enormous values even in those cases where such "unsymmetrically" arranged substitutes are all *chemically identical*. But it appears, that for the occurrence of the crystal-enantiomorphism, the *chemical inequality* of these substitutes is a very predominant factor: and from this fact the significance of LE BEL'S and VAN 'T HOFF'S "unsymmetrical atoms" for the whole problem has now become somewhat more comprehensible.

For in the question considered evidently *two* influences must properly be distinguished: *a*) that of the spacial configuration, which differs from its mirror-image, independently of whether the substitutes are equal or unequal, and whether the molecule possesses any other symmetry-elements (only axes of the first class); and *b*) the greater or smaller chemical differences of the substitutes, which are arranged in the manner, indicated sub *a*). The influence sub *a*) appears principally to cause the phenomenon of *optical activity*; that sub *b*) the more or less evident *enantiomorphism* of the crystalline structure, and the resulting polarity of homologous directions in it. Evidently the case of the "unsymmetric atoms" has thus to be considered only as *an extremely favourable opportunity* for the occurrence of the complete phenomenon, which is formulated in PASTEUR'S principle: here these influences are superposed, the one upon the other, because in most cases where the circumstances mentioned sub *b*) are present, those indicated sub *a*) will also be present. If the influence mentioned sub *b*) is *not* present, but only that sub *a*), — and this occurs precisely in the simple case of the complex cobalti-salts here studied, — then the enantiomorphous structure can be revealed eventually in the solid state, but it can evidently also be totally absent under the simultaneous influence of other factors. In our case the special nature of the electronegative part (anion) of the molecule seems to belong to these special circumstances: for the enantiomorphism of the crystalline structure seems

clearly to reveal itself only in the case of those cobalti-salts whose anions contain several *oxygen*-atoms.<sup>1)</sup>

It must be proved by future investigations, in how far this influence of the oxygen-containing radicals may be considered as a general and essential one; and if general, of what nature it actually is.

In any case it has now become clear that in the phenomenon discovered by PASTEUR, the optical activity of the molecules at the one side, and the enantiomorphism of the crystalforms, as well as the phenomena connected therewith regarding the pyro- and piezo-electric properties, — do *not* play an equivalent role. More detailed and more extensive investigations in this same direction will perhaps be able to teach us more exactly than now, what share the special configuration of the molecules really possesses for the occurrence of each of these categories of physical phenomena.

Groningen, March 1915. *Laboratory for Inorganic Chemistry  
of the University.*

**Chemistry.** — “*The Allotropy of Bismuth.*” II. By Prof. ERNST COHEN.

(Communicated in the meeting of March 27, 1915).

1. In my first paper<sup>2)</sup> on this matter (published in collaboration with Mr. A. L. TH. MOESVELD) we pointed out that bismuth can be transformed into a second allotropic modification at 75° C., and that this metal as it has been known up to the present is a metastable system at ordinary temperatures, in consequence of the marked retardation which accompanies that transformation.

2. However, the results obtained with cadmium, copper, antimony etc. gave rise to the supposition that in this case also the previous thermal history of the metal might have an influence on the transition temperature, which would prove that there exist more than two forms of bismuth.

3. Our dilatometric measurements carried out in order to clear up this point more fully were made in the same way as in the experiments with cadmium<sup>3)</sup>.

<sup>1)</sup> In this connection it may be remarked that such enantiomorphism as the *nitrates* and *perchlorates* possess, could also be stated in the case of the rhombic *dithionates* ( $(S_2O_6)''$ -ions). However the crystals of this salt contain much water of crystallisation, and effloresce so rapidly, that no exact measurements could be made. It is for that reason, that the salts are not described in paper II.

<sup>2)</sup> Zeitschr. f. physik. Chemie **85**, 419 (1913).

<sup>3)</sup> Proc. **16**, 485 (1913).

4. After having reduced the metal (500 grms. "Wismuth KAHILBAUM") to a fine powder, we studied its behaviour in a dilatometer. The metal had *not* undergone any previous treatment with an electrolyte. At 70° C. there did *not* occur any transformation.

5. After this the bismuth was kept in contact with a solution of potassium chloride (10 per cent) during 12 hours, and put again into a dilatometer. The results are given in Table I. The values indicated with *A* represent the duration of the observations (minutes), those indicated with *B* the level on the millimeter scale.

TABLE I.

70°.0		81°.0		90°.0		96°.0	
<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>
0	382	0	275	0	192	90	207
15	190	45	160	20	187	40	155
32	64	65	120	80	176	210	161
45	0	90	94	—	—	290	164

6. Comparing these measurements with those carried out formerly<sup>1)</sup> with a preparation of different previous thermal history (see table II) it is evident that there exist more than two forms of bismuth.

TABLE II.

Temperature	Duration of the observations in hours	Rise of the level in mm.
99.7	20	+ 450
93.7	2	+ 16
87.7	13	+ 12
77.7	30	+ 16
75.7	24	+ 10
74.7	14	— 10
15	36	— 95

Whilst we found formerly (Table II) at 81° and 90° an *increase* of volume, we now find a *decrease* (Table I) at these temperatures.

<sup>1)</sup> Zeitschr. f. physik. Chemie **85**, 419 (1913).

7. These results are corroborated by the observations made at 96°.0 C. (Table I); there occurs a *change* in the direction of motion of the meniscus at a constant temperature.

8. I hope to report shortly on the limits of stability of the different modifications.

*Utrecht*, March 1915.

VAN 'T HOFF-Laboratory.

**Chemistry.** — "*The Metastability of the Metals in consequence of Allotropy and its Significance for Chemistry, Physics, and Technics.*" IV. By Prof. ERNST COHEN and Mr. W. D. HELDERMAN.

(Communicated in the meeting of March 27, 1915).

*On the necessity of redetermining the data of Thermochemistry.* I.

1. Since our investigations as well as those of our collaborators have proved that the metals are metastable systems in consequence of the fact that different allotropic modifications of these substances may be simultaneously present, we wish to consider here some conclusions which may have an important bearing on thermochemistry.

*a. Heats of Reaction.*

2. The heat developed when a definite quantity of a metal reacts with any other substance, will be a function of the previous thermal treatment of the metal, as the relative quantities of the  $\alpha$ -,  $\beta$ -,  $\gamma$ -, ... modifications present in the metal are dependent on that treatment.

For instance, a definite quantity of cadmium (chemically pure) formed from the molten metal and which we shall indicate by the symbol  $M_1$ , will develop a different quantity of heat when it combines with any other substance than the same quantity of cadmium ( $M_2$ ) will do which has been formed at ordinary temperatures by electrolysis of the solution of a cadmium salt.

While  $M_1$  contains unknown quantities of  $\alpha$ -,  $\beta$ -,  $\gamma$ -cadmium,  $M_2$  consists of pure  $\gamma$ -cadmium; moreover we know to-day that the heat of transformation (per gram atom) of  $\gamma$ -cadmium  $\rightarrow$   $\alpha$ -cadmium is 739 gram calories at 18° C. <sup>1)</sup>

If, for instance, equal quantities of  $M_1$  and  $M_2$  are dissolved at 18° C. in equal quantities of HCl. 200 H<sub>2</sub>O, the evolution of heat which accompanies this reaction will be in maximo 739 gram calories

<sup>1)</sup> Proc. **17**, 1050 (1915).

higher in the case of  $M_2$  than in that of  $M_1$ . Such will be the case if  $M_1$  consists entirely of  $\alpha$ -cadmium. If  $\beta$ - and  $\gamma$ -cadmium are simultaneously present (this represents the general case) the difference will be less than 739 gram calories per gram atom.

4. TH. W. RICHARDS and BURGESS<sup>1)</sup> found that the heat of reaction between  $\text{HCl} \cdot 200 \text{H}_2\text{O}$  and cadmium which has been electrolytically deposited, ( $\gamma$ -cadmium) is 17200 gram calories (at  $20^\circ \text{C}$ .) per gram atom of the metal. In this case the error would be 4.3% in maximo. But even if it should reach only a small fraction of this value it would surpass the experimental errors, as thermochemical measurements can be carried out to-day with a precision of some tenths of one per cent. From this we may conclude that the presence of the different modifications must be taken into account.

Up to the present this could not be done, so that all the heats of reaction of the metals determined hitherto are to be considered as *fortuitous* values.

5. This is also true of the figures found by JULIUS THOMSEN<sup>2)</sup> for the heat of reaction of cadmium with different solutions of  $\text{HCl}$ , as he used the metal in the form of plates. The metal had been melted and consequently contained unknown quantities of  $\alpha$ -,  $\beta$ -,  $\gamma$ -cadmium<sup>3)</sup>.

6. What has been said here concerning cadmium evidently holds also for the other metals.

7. All thermochemical values which have been calculated on the basis of these erroneous values, evidently include the same errors: they are *fortuitous* values.

8. The measurements of TH. W. RICHARDS and BURGESS, cited above, which have been partly redetermined by E. E. SOMERMEIER<sup>4)</sup>, indicate that the previous thermal treatment of the metal experimented with plays a rôle.

As these results are not strictly comparable amongst themselves, we shall not discuss them here.

9. The true heats of reaction of the metals, which represent

<sup>1)</sup> Journ. Americ. Chem. Soc. **32**, 431, 1176 (1910).

<sup>2)</sup> Thermochemische Untersuchungen **3**, 277 Leipzig (1883). Comp. TH. W. RICHARDS and BURGESS, Journ. Americ. Chem. Soc. **32**, 431 (1910).

<sup>3)</sup> Comp. our paper Zeitschr. f. physik. Chemie **89**, 287 (1915).

<sup>4)</sup> Phys. Rev. (2) **1**, 141 (1913).

strictly defined and reproducible values are not known up to the present; they must be determined using the pure  $\alpha$ -,  $\beta$ -,  $\gamma$ -, . . . modifications of the metals.

*b. Latent heat of fusion.*

10. If a molten metal solidifies at temperatures more or less below its melting point, there may be formed different modifications which remain simultaneously present after solidification. From this we may conclude a priori that different observers will find different values for the latent heat of fusion of that metal. These values will be a function of the thermal history of the specimen experimented with, this history depending on the special conditions of the experiment.

11. In other words if a definite quantity of a molten metal solidifies, the heat effect will be a function of the quantities of the  $\alpha$ -,  $\beta$ -,  $\gamma$ -, . . . modifications, which are formed during solidification.

As the heats of transformation are of the same order as the latent heats of fusion, we may expect large differences in the case of different observers, owing to the varying circumstances of the experiments.

For instance the latent heat of fusion of cadmium is said to be 13.7 gram calories per gram<sup>1)</sup>, whilst we found<sup>2)</sup> the heat of transformation of  $\gamma$ -cadmium into  $\alpha$ -cadmium to be 6.6 gram calories per gram at 18° C.

12. Reviewing the literature, we have found indeed (comp. Table I p. 1241) that there exist very marked differences.

While they reach 20 per cent in the case of lead, they are as high as 80 per cent in the case of sodium.

13. Without doubt these deviations are partly to be attributed to the presence of impurities in the metals experimented with, while the influence of errors of thermometry is also to be taken into account. These errors cannot however give rise to the differences shown in the table. We hope to report shortly on this question in detail.

14. From what has been said above it is evident, that the latent heats of fusion of the metals known hitherto as well as their heats of reaction and other data calculated from these values must be redetermined with the pure  $\alpha$ -,  $\beta$ -,  $\gamma$ -, . . . modifications of the metals.

<sup>1)</sup> Ann. de chim. et de phys. (3) **24**, 274 (1848).

<sup>2)</sup> Proc. **17**, 1050 (1915).

TABLE I.  
Latent heat of Fusion in gram calories per 1 gram of metal.

Metal	Latent heat of fusion	Author	Largest difference in percentages
Potassium	15.7	JOANNIS <sup>1)</sup>	16
	13.61	BERNINI <sup>2)</sup>	
Lead	5.86	RUDBERG <sup>3)</sup>	20
	5.37	PERSON <sup>4)</sup>	
	5.37	MAZZOTTO <sup>5)</sup>	
	5.32	SPRING <sup>6)</sup>	
	6.45	ROBERTSON <sup>7)</sup>	
Sodium	31.7	JOANNIS <sup>1)</sup>	80
	17.75	BERNINI <sup>2)</sup>	
	27.5	EZER GRIFFITHS <sup>8)</sup>	
Tin (white)	13.3	RUDBERG <sup>3)</sup>	10
	14.25	PERSON <sup>4)</sup>	
	14.65	SPRING <sup>6)</sup>	
	13.6	MAZZOTTO <sup>5)</sup>	
	14.05	ROBERTSON <sup>7)</sup>	

Utrecht, March 1915.

VAN 'T HOFF-Laboratory.

**Physics.** — “*On the Kinetic Interpretation of the Osmotic Pressure.*”  
By Prof. P. EHRENFEST. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of March 27, 1915).

The fact that the dissolved molecules of a diluted solution exert on a semi-permeable membrane in spite of the presence of the solvent exactly the same pressure as if they alone were present and that in the ideal gas state — this fact is so startling that attempts have

<sup>1)</sup> Ann. de chim. et de phys. (6) **12**, 381 (1887).

<sup>2)</sup> Nuov. Cim. (5) **10**, 1 (1905); Physik. Zeitschr. **7**, 168 (1906).

<sup>3)</sup> Pogg. Ann. **19**, 133 (1830).

<sup>4)</sup> Ann. de chim. et de phys. (3) **24**, 129 (1848).

<sup>5)</sup> Mem. Ist. Lombardo **16**, 1 (1891).

<sup>6)</sup> Bulletin Acad. Roy. de Belg. (3) **11**, 400 (1886).

<sup>7)</sup> Journ. chem. Soc. **81**, 1233 (1902).

<sup>8)</sup> Proc. Roy. Soc. London **89**, (A) 119, (1914).

been repeatedly made to get a kinetic interpretation that was as lucid as possible. With regard to its contents the following discussion is closely connected with the well-known work of L. BOLTZMANN<sup>1)</sup>, H. A. LORENTZ<sup>2)</sup>, O. STERN<sup>3)</sup>, G. JÄGER<sup>4)</sup>, and particularly that of P. LANGEVIN<sup>5)</sup><sup>6)</sup>. By making use of the virial thesis and of the remarkable property which is further on formulated by equation (1), it is, however, possible to simplify the derivation.

Let in an infinitely extended mass of water through a closed surface  $\Omega$  a region  $G$  of the volume  $V$  be distinguished by the following definition: let inside  $\Omega$  besides the water molecules ( $W$ ) also  $n$  sugar molecules ( $S_1 \dots S_h \dots S_n$ ) be present, outside it only watermolecules. The surface  $\Omega$  may possess the following properties (of a "semi-permeable membrane"): whenever the centre of gravity of a molecule  $S$  is about to pass through  $\Omega$ , the molecule is perfectly elastically reflected by  $\Omega$ ;  $\Omega$  does not exert any forces on the molecules  $W$ , however. We want to know the pressure  $P$  (osmotic pressure), which  $\Omega$  experiences per  $\text{cm}^2$  through the collisions of the sugar molecules.

CLAUSIUS' *virial thesis*, applied only to the sugar molecules, requires that:

$$2\bar{L} + \sum_h \overline{(X_h x_h + Y_h y_h + Z_h z_h)} = 0 \dots \dots (A)$$

Here

$x_h, y_h, z_h$  are the coordinates of the centre of gravity of the  $h^{\text{th}}$  sugar molecule at an arbitrary moment  $t$ ;

$X_h, Y_h, Z_h$  are the resultants<sup>7)</sup> of all forces acting at the moment  $t$  on the  $h^{\text{th}}$  sugar molecule;

$L$  the kinetic energy of the translation of all the molecules  $S$  added together at the moment  $t$ .

The horizontal line expresses: taking a mean of a very long time  $\theta$ .

Let us now follow the  $h^{\text{th}}$  molecule  $S$  during the time  $\theta$ . The force  $X_h, Y_h, Z_h$  on the  $h^{\text{th}}$  molecule is owing to three causes:

1. to the collisions on the surface  $\Omega \rightarrow X_h', Y_h', Z_h'$ ;

2. to the attraction and repulsion by all the other molecules  $S \rightarrow X_h'', Y_h'', Z_h''$ ;

<sup>1)</sup> L. BOLTZMANN, Z. f. ph. Ch. **6** (1890) 474; **7** (1891) 88. [Wiss. Abh. N<sup>o</sup>. 93, 94].

<sup>2)</sup> H. A. LORENTZ, Z. f. ph. Ch. **7** (1891) 36. [Abbandl. I, p. 175].

<sup>3)</sup> O. STERN, Z. f. ph. Ch. **81** (1912) 441.

<sup>4)</sup> G. JÄGER, Ann. de Phys. **41** (1913) 854.

<sup>5)</sup> P. LANGEVIN, Journ. Ch. phys. **10** (1912) 524; 527.

<sup>6)</sup> Cf. also PH. KOHNSTAMM, These Proc. 7, 729.

<sup>7)</sup> We suppose for the sake of simplicity that the molecules are centres of force of one dimension.

3. to the attraction and repulsion by all the molecules  $W \rightarrow X_h''', Y_h''', Z_h'''$ .

During the greater part of  $\theta$  the  $h^{\text{th}}$  molecule  $S$  is found in volume elements far inside the region  $G$ , and only during a very small part of  $\theta$  in the periferic volume elements of  $G$  close to the surface  $\Omega$ . Let us now first direct our attention to a volume element  $dx dy dz$  far in the interior of the region  $G$ , far from  $\Omega$ . Repeatedly the molecule  $S_h$  is found for a short time in this element.

In this we find that:

$$X_h'' + X_h''', Y_h'' + Y_h''', Z_h'' + Z_h'''$$

assumes now positive, now negative values of rapidly varying amount, and — because we are far from  $\Omega$ , in the midst of the homogeneous solution — equally frequently equally large positive as negative values. Because besides  $X_h', Y_h', Z_h'$  are always zero, it is clear that the mean contribution to the virial yielded by the  $h^{\text{th}}$  molecule  $S$ , i. e.  $S_h$ , during its residence in an “internal” volume element  $dx dy dz$  of the region  $G$ , is:

$$dx dy dz [x \bar{X}_h + y \bar{Y}_h + z \bar{Z}_h] = 0 \quad . \quad . \quad . \quad (1)^1$$

and likewise for every “internal” volume-element. This is no longer the case for “peripheric” volume elements close to the surface  $\Omega$ . Here in the direction of the normal to  $\Omega$  the symmetry is disturbed:

1. The force exerted at the impact by  $\Omega$  on the molecule  $S_h$  is always directed inward;

2. The joint molecules  $S$ , which act on  $S_h$  all lie on *one* side of  $\Omega$  (the inside);

3. On account of the presence of the molecules  $S$  the concentration of the water on the inside of  $\Omega$  is different from that on the other side.

Let us now add the contributions yielded by *all* the molecules  $S$  during their presence in all the “peripheric” volume elements to the second term of the equation (A): Thus we get corresponding to the above mentioned three kinds of forces an expression with three terms:

$$\sum_h (X_h x_h + Y_h y_h + Z_h z_h) = W' + W'' + W''' \quad . \quad . \quad . \quad (2)$$

*If the concentration  $C_s$  of the molecules decreases to zero,  $W'$  becomes small of the same order of magnitude as  $C_s$ , on the other hand  $W''$  and  $W'''$  of higher order.*

<sup>1)</sup> We draw attention to the fact, that this holds as well for repulsive as for attractive forces.

It should be namely borne in mind that:

*First of all* all the three  $W$ 's become smaller already on account of this that in (2) the  $\sum_k$  must be taken over a number of molecules  $S$ , which decreases in direct ratio with  $c_s$ .

*Secondly*, however,  $W''$  decreases *besides* on account of this that the forces  $X_k''$ ,  $Y_k''$ ,  $Z_k''$  which a certain molecule  $S$  experiences from all the other molecules  $S$ , decreases at the same time with the number of the latter to zero, likewise  $W'''$ , because the *difference* of the concentrations of the molecules  $W$  on the two sides of  $\Omega$ , which determines  $x\overline{X''}$ ,  $y\overline{Y''}$ ,  $z\overline{Z''}$ , decreases to zero at the same time with  $c_s$ . For  $W'$ , which arises from the collisions of the molecules  $S$  with  $\Omega$ , there does not exist an analogous *second* reason to approach zero.

If therefore in the case of *diluted* solutions we confine ourselves in equation (A) to terms of the first order in  $c_s$ , we have:

$$2L + W' = 0. \quad \dots \quad (A')$$

One can now easily convince oneself that this expresses that the dissolved molecules  $S$  exert on  $\Omega$  the same pressure as when they were only enclosed in  $\Omega$  and that as an ideal gas.  $W'$  can namely be calculated from the pressure  $P$  exerted by  $\Omega$  on the sugar molecules, and becomes:

$$w' = -3PV \quad \dots \quad (3)^1$$

Further:

$$2L = 2.3 n \alpha T \quad \dots \quad (4)$$

when  $\alpha T$  is the mean kinetic energy per degree of freedom.

If we take particularly one gramme molecule of sugar, i.e.  $n$  equal to the Avogadro value  $N$ , and put

$$N 2 \alpha T = RT \quad \dots \quad (5)$$

(A') passes into:

$$PV = RT \quad \dots \quad (6)$$

VAN 'T HOFF'S equation for the osmotic pressure of a dilute solution.

The deviations from equation (6) for solutions which are no longer exceedingly diluted, have been repeatedly treated *thermodynamically*.<sup>2)</sup> O. STERN has tried to give a purely kinetic treatment in analogy with the kinetic theory of non-ideal gases.<sup>3)</sup> Compare also

<sup>1)</sup> Comp. the perfectly analogous calculation for ideal gases L. BOLTZMANN. Gastheorie II, p. 143, § 50.

<sup>2)</sup> VAN LAAR: Z. f. phys. Ch. 15 (1894) 457; "6 Vorträge" (1906); VAN DER WAALS and KOHNSTAMM, Lehrbuch d. Thermodynamik.

<sup>3)</sup> loc.cit.

the indications given by LANGEVIN.<sup>1)</sup> For the experimental investigation we may refer to FINDLAY "Der osmotische Druck" (Dresden 1914).

*Remarks.*

For the pressure on a semi-permeable membrane in the case of very dilute solutions it is, as we see immaterial whether or no there is interaction between the molecules  $S$  and the molecules  $W$ . Certain other effects of the osmotic pressure, can, however, only be brought about in consequence of such interaction: e.g. the difference of level that comes about between the solution and the pure water, when they are in tubes open at the top, and are in communication through a semi-permeable membrane. Let us consider the following imaginary case: The "sugar" molecules have no interaction at all with the water molecules. It is clear that there cannot ensue a difference of level — the sugar simply evaporates from the solution. When a glass bell-jar is put over the two communicating tubes, the following state of equilibrium is obtained: two solutions of the same concentration on either side with an equally high level. If the two tubes are placed each under a bell-jar of its own, sugar-vapour is formed over the solution with a pressure of the same value as the osmotic pressure of the solution and no difference of level appears then either.

If the difference in level in question is to make its appearance, none of the three following factors can, indeed, be omitted: first the tendency of the sugar to spread (its kinetic pressure), secondly the cohesion of the water, thirdly the interaction of the molecules  $S$  and  $W$ , without which it would not be possible for the sugar to lift up the water.

**Mathematics.** — "*On NÖTHER'S theorem*". By Dr. W. VAN DER WOUDE. (Communicated by Prof. JAN DE VRIES).

(Communicated in the meeting of March 27, 1915).

§ 1. BRILL and NÖTHER'S well-known paper on algebraic functions<sup>2)</sup> has as starting-point a theorem<sup>3)</sup> shortly before pronounced by NÖTHER. Its meaning may principally be indicated as follows:

"A curve  $F_2$  may be represented by the form

$$F_3 \equiv AF_1 + BF_2,$$

<sup>1)</sup> loc. cit.

<sup>2)</sup> Math. Annalen, 7 (p. 271.)

<sup>3)</sup> Math. Annalen, 6 (p. 351): "Ueber einen Satz aus der Theorie der algebraischen Funktionen."



The second determinant is deduced from the first by multiplying the terms of the first column by  $x^{m+n-1}$ , those of the second by  $x^{m+n-2}$ , . . . , and by adding them afterwards to those of the last column. At the same time appears from this the well-known identity:

$$\varrho \equiv PF_1 + QF_2, \dots \dots \dots (4)$$

in which  $P$  and  $Q$  are of no higher order than  $(n-1)$  and  $(m-1)$  in  $x$ .

Let now  $F_3$  be an arbitrary integral function of  $x$  and  $y$  of degree  $r$  in  $x$  ( $r \geq m, r \geq n$ ); we arrange  $F_1, F_2$  and  $F_3$  according to the descending powers of  $x$  and divide  $F_3$  by  $F_1F_2$ , let us call the quotient  $q$  and the rest  $F'_3$ , then

$$F_3 \equiv q F_1 F_2 + F'_3. \dots \dots \dots (5)$$

The function  $F'_3$  is in  $x$  of no higher order than  $(m + n - 1)$ .

From (4) follows

$$\varrho F'_3 \equiv PF'_3 F_1 + QF'_3 F_2 \dots \dots \dots (6)$$

The terms in the second member whose degrees in  $x$  are higher than  $(m + n - 1)$  must disappear.

If we therefore divide  $PF'_3$  and  $QF'_3$  by  $F_1F_2$ , after arrangement according to the descending powers of  $x$ , the quotients will be each other's opposites.

Hence:

$$\begin{aligned} PF'_3 F_1 &\equiv q_1 F_1 F_2 + R F_1 \\ QF'_3 F_2 &\equiv -q F_1 F_2 + S F_2 \end{aligned}$$

By this (6) is reduced to

$$\varrho F'_3 \equiv R F_1 + S F_2, \dots \dots \dots (7)$$

in which  $R$  and  $S$  are of no higher degree than  $(n-1)$  and  $(m-1)$  in  $x$ .

From this identity NÖTHER'S theorem is simply and generally to be deduced.

§ 3. We suppose now *provisionally* that all the points of intersection of  $F_1$  and  $F_2$  are simple ones. Is  $F_3 = 0$  the equation of a curve passing through all the points of intersection of  $F_1$  and  $F_2$ , the same is true according to (5) for the curve represented by  $F'_3 = 0$ . We will prove that now in the identity

$$\varrho F'_3 \equiv R F_1 + S F_2 \dots \dots \dots (7)$$

the functions  $R$  and  $S$  are divisible by  $\varrho$ .

We take for convenience sake one of the points of intersection 0 as origin of our system of coordinates,  $y$  is then a factor of  $\varrho$ . As  $F'_3$  also passes through 0,  $\varrho F'_3$  has a node in 0; while  $F_1$  and  $F_2$  possess only simple points there with different tangents. This is only possible if  $R$  and  $S$  also pass through 0.

Further has  $F_1'$  apart from 0 moreover  $(m-1)$  points of intersection with the  $X$ -axis, which intersections do not lie on  $F_2$ , so they do on  $S$ ; in the same way the points of intersection of  $F_2'$  with the  $X$ -axis lie to the number of  $(n-1)$  on  $R$ .

Now the  $X$ -axis has already  $n$  points of intersection with  $R$ , and  $m$  points of intersection with  $S$  all situated in the finite while  $R$  and  $S$  are respectively of degree  $(n-1)$  and  $(m-1)$  in  $x$ . So  $R$  and  $S$  are both divisible by  $y$ . We may, however, prove in the same way that  $R$  and  $S$  are divisible by all the other factors of  $y$ , so that we find :

$$F_3' \equiv RF_1 + SF_2 \dots \dots \dots (8)$$

From (5) it further ensues

$$F_3 \equiv AF_1 + BF_2 \dots \dots \dots (9)$$

§ 4. The preceding proof undergoes only a slight change if  $F_1$  and  $F_2$  show contact in one or more of their points of intersection, or possess multiple points there. We suppose in the first place that  $F_1$  and  $F_2$  touch each other in a point 0, which we again take as origin of the system of coordinates; moreover that  $F_3'$  too has in that point the same tangent  $l$  as  $F_1$  and  $F_2$ .

Let us now again consider the identity

$$\varrho F_3' \equiv RF_1 + SF_2 \dots \dots \dots (7)$$

If we suppose that the curves  $R$  and  $S$  do not both pass through 0, we might determine by  $RF_1$  and  $SF_2$ , which have in 0 a tangent  $l$  in common, a pencil of which one of the curves  $K$  has a node in 0;  $K$  would however not be touched by  $l$  in that case.

For in that case  $K$  would have one point of intersection more there with  $RF_1$  or  $SF_2$  than these two possess there between them. Now  $\varrho F_3'$  is a curve, however, from the pencil determined by  $RF_1$  and  $SF_2$  and one of its tangents in 0 coincides with the common tangent of  $F_1$  and  $F_2$ . Consequently  $R$  and  $S$  must pass through 0.

As in § 3 it appears further that  $R$  and  $S$  are divisible by  $y$  and by all the other factors of  $\varrho$ . Consequently the identities (8) and (9) remain in force.

In the same way it appears that (9) remains in force if  $F_1$  and  $F_2$  have in any point contact of higher order, provided that they show there contact of the same order with  $F_3'$  as well.

Let us finally suppose that in a point 0, which we again take as origin of the system of coordinates, the curve  $F_1$  possesses a  $p$ -fold,  $F_2$  a  $q$ -fold point; we provisionally suppose that  $F_1$  and  $F_2$  have

no common tangent in 0.  $F_3$  is supposed to pass through all the points of intersection of  $F_1$  and  $F_2$  and to possess in 0 a  $(p+q-1)$ -fold point; it is to be seen at once that the curve  $F_3'$  determined by (5) satisfies the same requirements.

Let us again consider the identity

$$\varrho F_3' \equiv R F_1 + S F_2 \dots \dots \dots (7)$$

The resultant  $\varrho$  contains the factor  $y^{pq}$ ;  $F_3'$  has no terms of a lower degree than  $(p+q-1)$ .

Let us write the equations of  $F_1$  and  $F_2$  thus:

$$F_1 \equiv (y - \alpha_1 x)(y - \alpha_2 x) \dots (y - \alpha_p x) + u_{p+1} + u_{p+2} + \dots + u_n = 0$$

$$F_2 \equiv (y - \beta_1 x)(y - \beta_2 x) \dots (y - \beta_q x) + v_{q+1} + v_{q+2} + \dots + v_n = 0,$$

in which  $\alpha_i \neq \beta_k$ ,

then it appears from (7) that the terms of the lowest degree in  $R$ , must at least be of degree  $q$ , those in  $S$  at least of degree  $p$ . For if  $R$  or  $S$  were of a lower degree the terms of the lowest degree in  $R F_1$  and  $S F_2$  could not neutralize each other and in  $R F_1 + S F_2$  terms of a lower degree than  $(p+q)$  must consequently occur. So  $R$  has a  $q$ -fold,  $S$  a  $p$ -fold point in 0.  $R$  passes moreover through all the points which  $F_2$  — to the number of  $(n-q)$  — has in common with the  $X$ -axis apart from 0; the function  $R$  contains therefore the factor  $y$ . At the same time  $y$  is a factor of  $S$  and so we may divide both members of (7) by  $y$ . After that we may however, follow the same reasoning once more and going on in that way, prove that both members of (7) are divisible by  $y^{pq}$ .

Consequently all the factors of  $\varrho$  are again divisible on  $R$  and  $S$  and in this case too we find again

$$F_3 \equiv A F_1 + B F_2 \dots \dots \dots (9)$$

To wind up with we may suppose that  $F_1$  possesses in 0 a  $p$ -fold point,  $F_2$  a  $q$ -fold, that they have moreover in 0 at one of the branches contact of an arbitrary order. Reasoning in the same way as above, we find, that even now the identity (9) remains in force, if only  $F_3$  has a  $(p+q-1)$ -fold point in 0 and moreover in 0 contact with  $F_1$  and  $F_2$  of the same order as they have between them.

*Observation.* We have supposed that in the points of intersection of  $F_1$  and  $F_2$  neither curve has a multiple point with coinciding tangents. NÖTHER has already shown how that case may be reduced to one of those treated here.

§ 5. If  $F_3$  is a curve of degree  $r$ , we can observe that the

curves  $A$  and  $B$  need at most be of degree  $(r-m)$  and  $(r-n)$ . If this is not the case, however, the terms of the highest degree of  $AF_1$  and  $BF_2$  will cancel each other; as the terms of the highest degree in  $F_1$  and  $F_2$  have no common factor, those of  $AF_1$  and  $BF_2$  will be divisible by those of  $F_1F_2$ .

Let us therefore suppose

$$\begin{aligned} AF_1 &\equiv A'F_1F_2 + A''F_1 \\ BF_2 &\equiv B'F_1F_2 + B''F_2, \end{aligned}$$

in which we extend the division by  $F_1F_2$  only so far that the terms of the highest degree in  $A'F_1$  and  $B'F_2$  have disappeared, we have

$$A' \equiv -B'.$$

So we find

$$F_3 \equiv A''F_1 + B''F_2,$$

in which  $A''$  and  $B''$  are of a lower degree than  $A$  and  $B$ . So we may go on till we find

$$F_3 \equiv A^{(c)}F_1 + B^{(c)}F_2$$

in which  $A^{(c)}$  and  $B^{(c)}$  are at most of degree  $(r-m)$  and  $(r-n)$ .

**Mathematics.** — “*A bilinear congruence of rational twisted quintics*”.

By PROFESSOR JAN DE VRIES.

(Communicated in the meeting of March 27, 1915).

1. The base-curves of the pencils belonging to a net  $[\Phi^3]$  of cubic surfaces form a *bilinear congruence*. For through an arbitrary point passes only *one* curve, and an arbitrary straight line is chord of *one* curve; for the involution  $I_2^3$ , which the net determines on that line, has *one* neutral pair of points.

We shall consider the particular net, the base of which consists of the twisted cubic  $\sigma^3$ , the straight line  $s$  and the points  $F_1, F_2, F_3$ .<sup>1)</sup> The surfaces  $\Phi^3$ , which connect this basis with a point  $P$  have moreover a twisted quintic  $\varrho^5$  in common. A *bilinear congruence*  $[\varrho^5]$  is therefore determined by  $[\Phi^3]$ . A plane passing through  $s$  intersects two arbitrary surfaces of the net in two conics; of their intersections three lie on  $\sigma^3$ , the fourth belongs to  $\varrho^5$ ; consequently this curve has four points in common with  $s$ , is therefore *rational*.

The straight line  $s$  is apparently a *singular quadrisequant*.

The figure consisting of  $s$ ,  $\sigma^3$  and  $\varrho^5$  is, as complete intersection

<sup>1)</sup> Two other particular nets I have considered in two communications placed in volume XVI (p. 733 and p. 1186) of these “*Proceedings*”. They determine bilinear congruences of twisted quartics (1st and 2nd species).

of two  $\Phi^3$ , of rank 36. As  $\sigma^3$  is of rank four and  $\varrho^5$  as rational curve of rank eight, while  $s$  has four points in common with  $\varrho^5$ ,  $\varrho^5$  and  $\sigma^3$  will have *eight* points in common. We can therefore determine the congruence  $[\varrho^5]$  as *the system of rational curves  $\varrho^5$  passing through three fundamental points  $F_1, F_2, F_3$ , cutting the singular curve  $\sigma^3$  eight times and having  $s$  as singular quadrisecant.*

It incidentally follows from this, that  $\varrho^5$  may satisfy 20 simple conditions.

2. Let  $\bar{b}$  be a bisecant of  $\sigma^3$ , resting on  $s$ ; all  $\Phi^3$  passing through a point of  $b$  have this line in common, therefore determine a pencil the base of which consists of  $s, b, \sigma^3$  and a *rational*  $\varrho^4$ , which has three points with  $s$  six points with  $\sigma^3$ , consequently *one* point in common with  $b$ .

There are also figures of  $[\varrho^5]$  consisting of a conic  $\varrho^2$  and a cubic  $\varrho^3$ . The plane  $\Phi_1$  passing through  $F_1$  and  $s$  forms with the ruled surface  $\Phi_1^2$ , determined by  $\sigma^3, F_2$  and  $F_3$ , a  $\Phi_1^3$ . Any other figure of  $[\Phi^3]$  intersects  $\Phi_1^3$  along a conic  $\varrho_1^2$  in the plane  $\Phi_1$ , passing through  $F_1$  and the intersections  $S_1^{(k)}$  of  $\sigma^3$ , and a twisted curve  $\varrho_1^3$  intersecting  $\sigma^3$  in five points  $C_1', C_1''$ , which are determined by  $\Phi_1^3$ ; it passes of course through  $F_2$  and  $F_3$ .

To the curves  $\varrho_1^3$  belong two degenerate figures each formed by the bisecant of  $\sigma^3$  out of one of the points  $C$ , and the conic  $\varrho_1^2$ , in which  $\Phi_1^2$  is intersected by the plane that connects the points  $F_2$  and  $F_3$  with the other point  $C$ . Apparently  $\varrho_1^2$  and the corresponding  $\varrho_1^3$  form a degenerate curve  $\varrho^4$ .

The three degenerate conics  $\varrho_1^2$  as well determine degenerate curves  $\varrho^4$ . For the straight line  $S_1' S_1''$  is a bisecant  $b$ ; hence the line  $F_1 S_1'''$  forms with the corresponding  $\varrho_1^3$  a degenerate figure  $\varrho^4$ .

3. To the net  $[\Phi^3]$  belongs the surface  $\Sigma^3$ , which has a node in a point  $S$  of  $\sigma^3$ . This nodal surface determines with any other surface of the net a  $\varrho^5$ , intersecting  $\sigma^3$  in  $S$ , is therefore the locus of the  $\varrho^5$  passing through the *singular point*  $S$ .

The surfaces  $\Sigma_1^3$  and  $\Sigma_2^3$  have  $s, \sigma^3$  and a  $\varrho^5$  in common, consequently *one*  $\varrho^5$  passes through two points  $S_1, S_2$  of  $\sigma^3$ . The groups of eight points, which the curves of the congruence determine on  $\sigma^3$  form therefore an involution of the second rank. From this ensues that  $\sigma^3$  is osculated by 18 curves  $\varrho^5$ , and contains 21 pairs  $S_1, S_2$  through which  $\infty^1$  curves  $\varrho^5$  pass. So there are 21 surfaces  $\Phi^3$  each possessing *two* nodes lying on  $\sigma^3$ .

A straight line passing through the vertex  $S$  of the *monoid*  $\Sigma^3$  inter-

sects the latter moreover in a point  $P$  and the plane  $q$  passing through  $F_1, F_2, F_3$  in a point  $P'$ , which we shall consider as an image of  $P$ . As *one*  $q^5$  passes through any point  $P$ , the curves of the congruence lying on  $\Sigma^3$  are represented by a pencil of rational curves  $q^4$ . Every  $q^4$  has in common with the intersection  $q^3$  of  $\Sigma^3$  the five points, in which the corresponding  $q^5$  intersects the plane  $q$ ; the remaining seven intersections of  $q^3$  with  $q^4$  are base-points of the pencil ( $q^4$ ). To them belong the points  $F_1, F_2, F_3$ ; the remaining four are intersections of four straight lines lying on  $\Sigma^3$ . One of them is intersected by every  $q^5$  in  $S$  and in a point  $P$ , is therefore a *singular bisecant*  $p$  of the congruence; the involution which the  $\infty^1$  curves  $q^5$  determine on it, is parabolic; so we might call  $p$  a *parabolic bisecant*. The remaining three straight lines  $d_1, d_2, d_3$  passing through  $S$  are common trisecants of the curves  $q^5$ ; on these *singular trisecants* as well the involution of the points of support is special, for each group contains the point  $S$ .

The monoid  $\Sigma^3$  contains moreover two straight lines passing through  $S$  viz. the two bisecants of  $\sigma^3$  cutting  $s$ , being consequently component parts of two  $q^5$  degenerated into a straight line  $b$  and a  $q^4$ .

The pencil ( $q^4$ ) has three double base-points  $D_1, D_2, D_3$  and four single base-points  $E, F_1, F_2, F_3$ ; it contains six compound figures: three figures consisting of a nodal  $q^3$  and a straight line and three pairs of conics.

Let us now first consider the figure formed by the straight line  $D_2D_3$  and the  $q^3$ , which has a nodal point in  $D_1$  and passes through the remaining six base-points. It is the image of a figure consisting of a bisecant  $b$  and a rational curve  $q^4$ ; for the plane passing through  $d_2$  and  $d_3$  has only one straight line in common with  $\Sigma^3$  so that  $D_2D_3$  cannot be the image of a conic passing through  $S$ . Consequently there lie on  $\Sigma^3$  three straight lines  $b$  not passing through  $S$ , and therefore three curves  $q^4$  passing through  $S$ .

The conic passing through  $D_1, D_2, D_3, E, F_1$  is the image of the conic  $q^2$  which the plane  $(F_1s)$  has in common with  $\Sigma^3$ ; the conic to be associated to her passing through  $D_1, D_2, D_3, F_2, F_3$  is the image of the  $q^3$  forming with  $q^2$  a curve of the congruence [ $q^5$ ]. There are apparently there figures ( $q^3, q^2$ ) on  $\Sigma^3$ .

4. The curves  $q^5$ , meeting  $s$  in a point  $S^*$  lie on the nodal surface  $\Phi^3$ , which has  $S^*$  as node. The monoids  $\Sigma^{*3}$  belonging to two points of  $s$ , have *one*  $q^5$  in common; so the groups of four points which the  $q^5$  have in common with  $s$  form a  $I_2^4$ . There are consequently six  $q^5$  which osculate  $s$ , and three binodal surfaces  $\Phi^3$  which

have their nodes on  $s$ , consequently contain  $\infty^1$  curves  $\varrho^5$ , intersecting  $s$  in the same two points.

The  $\varrho^5$  of the monoid  $\Sigma^{*3}$  are represented on the plane  $\sigma \equiv F_1 F_2 F_3$  by a pencil of  $\varrho^4$ , which have the intersection  $D$  of  $s$  as triple point and pass through  $F_1, F_2, F_3$ . The remaining base-points  $E_1, E_2, E_3, E_4$  of that pencil lie in the intersections of straight lines  $\rho_k$  of the monoid, which lines meet in  $S^*$  and apparently are parabolic singular bisecants. The sixth straight line of the monoid passing through  $S^*$  is the bisecant  $b$  of  $\sigma^3$ , consequently part of a degenerate  $\varrho^5$ .

The straight line  $DF_1$  is the image of the conic  $\varrho_1^2$ , in which the monoid is moreover intersected by the plane  $(sF_1)$ ; the nodal  $\varrho^3$  completing it into a  $\varrho^4$  represents the cubic  $\varrho^3$ , belonging to  $\varrho_1^2$ . So three figures  $(\varrho^3, \varrho^2)$  lie on  $\Sigma^{*3}$ .

The straight line  $DE_1$  forms with the nodal cubic passing through  $E_2, E_3, E_4, F_1, F_2, F_3$  and twice through  $D$ , the image of a degenerate  $\varrho^5$ , consisting of the straight line  $b$  in the plane  $(sp_1)$  and a rational  $\varrho^4$  passing through  $S^*$ . The monoid  $\Sigma^{*3}$  too contains therefore five figures  $(b, \varrho^4)$ .

5. We can now determine the order of the locus of the rational curves  $\varrho^4$ . It has  $s$  as quadruple straight line and passes thrice through  $\sigma^3$  (§ 3). Its intersection with a  $\Sigma^{*3}$  consists apart from these multiple lines of five curves  $\varrho^4$ , is therefore of order 33. *The rational curves  $\varrho^4$  lie therefore on a surface of order eleven.*

The section of this surface  $\Phi^{11}$  with the plane  $(F_1s)$  consists of the quadruple straight line  $s$ , and parts of degenerate figures  $\varrho^4$ . To it belong in the first place the three straight lines joining  $F_1$  to the intersections  $S_1^{(k)}$  of  $\sigma^3$  (§ 2); the remaining section is formed by the two  $\varrho_1^2$  belonging to the bisecants  $b$  out of the points  $C_1', C_1''$  (§ 2). A straight line passing through  $F_1$  intersects  $\Phi^{11}$  four times on  $s$  and has with each of the two conics  $\varrho_1^2$  a point of intersection not lying in  $F_1$ ; so five intersections lie in  $F_1$ . *The three fundamental points  $F$  are therefore quintuple points of  $\Phi^{11}$ .*

In order to determine the locus of the intersection  $B$  of a  $\varrho^4$  with the bisecant  $b$  coupled to it, we consider on  $s$  the correspondence between its intersections with  $b$  and  $\varrho^4$ . Through any point  $P$  passes one  $b$ ; to it are associated the three points  $Q$ , which  $\varrho^4$  has in common with  $s$ . In each point  $Q$ ,  $s$  is intersected by four curves  $\varrho^4$ ; hence four points  $P$  are associated to  $Q$ . From this it appears that  $s$  contains seven points  $B$ . A plane passing through  $s$  contains three straight lines  $b$ , consequently three points  $B$ ; so the

points  $B$  lie on a curve  $\beta^{10}$  with septuple secant  $s$ . In the same way it appears that  $\beta^{10}$  meets  $\sigma^3$  in 15 points. The surfaces  $\Phi^{11}$  and  $(b)^4$  have in  $s$  and  $\sigma^3$  a section of order  $4 + 3 \times 2 \times 3$ ; moreover they have  $\beta^{10}$  in common. The remaining section of order 12 must consist of straight lines belonging to degenerate figures  $\varrho^5$ , each composed of a  $\varrho^3$  and two straight lines  $b$  intersecting it. From this it ensues that  $[\varrho^5]$  contains six figures consisting of a twisted cubic and two of its secants.

This result may also be formulated in this way: through three points  $F_k$  pass 6 curves  $\varrho^3$  which intersect a given  $\sigma^3$  four times and a straight line  $s$  twice. Such a  $\varrho^3$  intersects the ruled surface  $(b)^4$  in two points  $B$  lying outside  $s$  and  $\sigma^3$ ; through these points pass the two straight lines  $b$ , completing  $\varrho^3$  into a  $\varrho^5$ .

6. Any straight line  $d$  having three points in common with a  $\varrho^5$  is a *singular trisecant* of the congruence. For through it passes one  $\Phi^3$  and the remaining surfaces of the net intersect it in the triplets of an involution. From this it ensues that the trisecants of the  $\varrho^5$  form a *congruence of order three*, as a  $\varrho^5$  is intersected in each of its points by three trisecants. In § 3 it has been proved that any point  $S$  of  $\sigma^3$  also sends out three straight lines  $d$ ; on these singular trisecants, however, all the groups of the  $I_3$  have the point  $S$  in common.

Let  $b$  be a bisecant of a  $\varrho^5$  intersecting  $\sigma^3$ . Through it passes one  $\Phi^3$ ; the net therefore determines on  $b$  an involution  $I^2$ , so that  $b$  is a *singular bisecant*.

Through a point  $P$  pass four straight lines  $b$ . For the curve  $\varrho_P^5$ , which can be laid through  $P$  is projected out of  $P$  by a cone  $k^4$ ; the latter has in common with  $\sigma^3$  the eight points in which  $\varrho_P^5$  rests on  $\sigma^3$ . The remaining four intersections lie on edges of  $k^4$ , which have in common with  $\varrho_P^5$  two points not lying on  $\sigma^3$ , consequently are *singular bisecants*.

These four straight lines  $b$  lie on the surface  $\Pi$ , which is the locus of the pairs of points, which the curves of  $[\varrho^5]$  have in common with their chords passing through the point  $P$ .  $\Pi$  is apparently a surface of order six with quadruple point  $P$ , the tangent cone of which coincides with  $k^4$ .

$\Pi^6$  contains  $s$  and  $\sigma^3$ , therefore has with an arbitrary  $\varrho^5$  four points of  $s$  and eight points of  $\sigma^3$  in common; of the remaining 18 points of intersection 12 lie on the 6 chords, which  $\varrho^5$  sends through  $P$ , and 6 in the points  $F$ . Hence  $\Pi^6$  has three nodes  $F_k$ .

With the cone  $k^4$   $\Pi^6$  has the curve  $q_{P^5}$  in common; the remaining section can only consist of straight lines. To it belong the *three* parabolic bisecants  $PF_k$  and the *four* singular bisecants  $b$ . From this it ensues that the three trisecants  $d$  which  $q_{P^5}$  sends through  $P$  are *nodal lines* of  $\Pi^6$ .

For a point  $S$  of the singular curve  $\sigma^3$  the surface  $\Pi^6$  degenerates into the monoid  $\Sigma^3$  and a cubic cone  $k^3$ , formed by singular bisecants  $b$ . The straight lines  $b$  form therefore a *congruence of order four, with singular curve  $\sigma^3$ , consequently of class nine*.

7. The surface  $A$  formed by the  $q^5$ , intersecting a straight line  $l$ , has the  $q^5$  intersecting  $l$  twice as *nodal curve*.

As  $l$  intersects every monoid  $\Sigma^3$  thrice,  $s$  and  $\sigma^3$  are *triple lines* on  $A$ . The section of  $A$  with the plane  $(F_1s)$  consists of the triple straight line  $s$  and three conics  $q_1^2$ ; of these, one passes through the intersection of  $l$ , the other two are determined by the two curves  $q_1^3$  resting on  $l$ . So  $A$  is a surface of *order nine, with triple points in  $F_1, F_2, F_3$* .

On  $A^9$  lie 15 straight lines, 9 conics, 9 curves  $q^3$  and 15 rational curves  $q^4$ . For  $l$  intersects 4 bisecants  $b$ , 11 curves  $q^4$ ; 3 conics and 6 curves  $q^3$ .

A plane  $\lambda$  passing through  $l$  intersects  $A^9$  along a curve  $\lambda^8$ ; the latter has in common with  $l$  the points, in which  $l$  is intersected by the  $q^5$ , which has  $l$  as bisecant. In each of the remaining six points  $\lambda$  is touched by a  $q^5$  of the congruence.

The locus of the points in, which a plane  $\varphi$  is touched by curves  $q^5$  is therefore a curve  $\varphi^6$ . It is the *curve of coincidence of the quintuple involution*, which determines  $[q^5]$  on  $\varphi$ . The intersections  $S^*, S_1, S_2, S_3$  of the singular lines  $s, \sigma^3$  are apparently *nodes* of  $\varphi^6$ .

With the surface  $A^9$  belonging to an arbitrary straight line  $l$ ,  $q^6$  has in those intersections  $4 \times 3 \times 2$  points in common; in each of the remaining intersections  $\varphi$  is touched by a  $q^5$  resting on  $l$ .

*The curves  $q^5$  touching  $\varphi$  form therefore a surface  $\Phi^{30}$ .*

A monoid  $\Sigma^3$  has in the points  $S^*, S_k$   $4 \times 2$  points in common with  $\varphi^6$ ; on  $\varphi^6$  lie therefore the points of contact of 10 curves  $q^5$  of the monoid. From this it ensues that  $s$  and  $\sigma^3$  are *decuple lines* of  $\Phi^{30}$ .

With the curve  $\varphi^6$ , belonging to the plane  $\psi$ ,  $\Phi^{30}$  has, in the four nodes of  $\varphi^6$ ,  $4 \times 2 \times 10$  points in common; in each of the remaining intersections  $\psi$  is touched by a  $q^5$ , which at the same time touches the plane  $\varphi$ . *There are consequently 100 curves  $q^5$ , touching two given planes.*

The plane  $\varphi$  has with  $\Phi^{30}$ , besides the curve of contact  $\varphi^6$  to be

counted twice, a curve  $\varphi^{18}$  in common possessing *four sextuple points* in  $S^*$ ,  $S_k$ . Apart from the multiple points,  $\varphi^6$  and  $\varphi^{18}$  have moreover  $6 \times 18 - 4 \times 2 \times 6$  points in common; from this it ensues that *each plane is osculated by thirty curves  $\varphi^5$* .

**Mathematics.** — “*Some particular bilinear congruences of twisted cubics.*” By Prof. JAN DE VRIES.

(Communicated in the meeting of March 27, 1915).

The bilinear congruences of twisted cubics  $\varrho^3$  may principally be brought to two groups.<sup>1)</sup> The congruences of the first group may be produced by two pencils of ruled quadrics, the bases of which have a straight line in common; the congruences of the second group consist of the base-curves of the pencils belonging to a net of cubic surfaces, which have in common a fixed point and a twisted curve of order six and genus three. REYER'S congruence formed by the  $\varrho^3$  passing through five given points  $F_k$ , belongs to both groups; it may be produced by two pencils of quadratic cones; the straight lines, connecting each of two points  $F_1, F_2$  with each of the remaining four, are base-edges. We shall now consider some other particular cases of congruences of the first group, which may also be produced by two pencils of quadratic cones.

1. We consider the curves  $\varrho^3$  passing through the *fundamental points*  $F_1, F_2, F_3, F_4$  and having the lines  $s_1$  (passing through  $F_1$ ) and  $s_2$  (passing through  $F_2$ ) as chords. Each  $\varrho^3$  is the partial intersection of a quadratic cone passing through the lines  $(s_1, F_1F_2, F_1F_3, F_1F_4)$ ;  $(s_2, F_2F_1, F_2F_3, F_2F_4)$ ; the congruence is consequently bilinear. Apparently  $s_1$  and  $s_2$  are *singular bisecants*. Any point  $S_1$  of  $s_1$  is singular; the  $\varrho^3$  passing through  $S_1$  lie on the cone of the second pencil passing through  $S_1$ . Consequently  $s_1$ , as well as  $s_2$ , is a *singular straight line of order two*.

The figures of the congruence consisting of a straight line  $d$  and a conic  $\sigma^2$ , may be brought to four groups.

A. The straight line  $d_{12} \equiv F_1F_2$ , may be combined with any  $\sigma^2$  of the system of conics passing through  $F_3$  and  $F_4$  and resting on

<sup>1)</sup> VENERONI, *Rendiconti del Circolo matematico di Palermo*, tomo XVI, 209—229. In a short communication in vol. XXXVII, 259, of the *Rendiconti del Ist. Lombardo*, VENERONI has added to these two main types a third which by the way may be considered as a limit case of the first type. This congruence may be produced by a pencil of quadrics and a pencil of quartic surfaces, one surface of which is composed of two quadrics of the first pencil. The bases of the pencils have a straight line in common, which is nodal line for the second pencil.

the three straight lines  $d_{12}, s_1, s_2$ . These curves lie on the hyperboloid  $H^2$ , which contains the three straight lines mentioned and the points  $F_3, F_4$  <sup>1)</sup>.

B. The straight line  $F_2 F_4 \equiv d_{24}$  may be coupled to any  $\sigma^2$  of the pencil in the plane  $(F_3 s_1)$ , which has the points  $F_1, F_3$  and the intersections of  $s_2$  and  $d_{24}$  as base-points. Similar systems of degenerate  $\sigma^3$  are determined by the straight lines  $d_{23}, d_{13}, d_{14}$  with pencils lying in the planes  $(F_4 s_1), (F_4 s_2), (F_3 s_2)$ .

C. The transversal  $g_3$  of  $s_1$  and  $s_2$  passing through  $F_3$  may be coupled to any  $\sigma^2$  of a pencil in the plane  $F_1 F_2 F_4$ ; the base consists of  $F_1, F_2, F_4$  and the intersection of  $g_3$ .

Analogously with this is the system determined by the transversal  $g_4$  of  $s_1, s_2$  through  $F_4$ ; the pencil lies in that case in the plane  $F_1 F_2 F_3$ .

D. In the plane  $F_1 F_3 F_4$  a pencil ( $\sigma^2$ ) is determined, the base of which consists of the intersection  $S_2$  of  $s_2$  and the points  $F_1, F_3, F_4$ . To each  $\sigma^2$  belongs a ray  $d$  of the pencil which has  $E_2$  as vertex and is situated in the plane  $(F_2 s_1)$ . In this system *both* component parts of  $(d, \sigma^2)$  are variable.

A system analogous with this is formed by the pencil of rays in the plane  $(F_1 s_2)$ , with vertex  $F_1$ , and a ( $\sigma^2$ ) in the plane  $F_2 F_3 F_4$ .

Summarising we observe that the figures  $\sigma^2$  form a locus of degree *ten*. In the general congruence of the first principal group the figures  $\sigma^3$  form also a surface of order ten; it does, however, not consist, as in this case, of different figures.

2. We can now easily determine the order of the surface  $\mathcal{A}$  formed by the  $\sigma^3$ , intersecting a given straight line  $l$ . For that purpose we observe that the intersection of  $\mathcal{A}$  with the plane  $F_1 F_2 F_3$  must consist of figures  $d$  and  $\sigma^2$ . To this belongs in the first place the  $\sigma^2$  of the pencil lying in this plane, which meets  $l$ ; further twice the straight line  $d_{12}$ , for  $l$  rests in its points of intersection with the hyperboloid  $H^2$  on two  $\sigma^2$ ; finally the two straight lines  $d_{13}, d_{23}$ , each belonging to a figure the  $\sigma^2$  of which rests on  $l$ . The intersection with  $F_1 F_2 F_3$  is therefore a figure of order six, passing four times through  $F_1$  and  $F_2$ , thrice through  $F_3$ .

The curves  $\sigma^3$  intersecting  $l$  consequently form a surface  $\mathcal{A}^6$ , having  $d_{12}$  as *nodal line*, passing through  $d_{13}, d_{23}, d_{14}, d_{24}$  and possessing

<sup>1)</sup> The conics passing through two points and resting on three arbitrary straight lines form a quartic surface. Here the planes  $F_3 F_4 F_1$  and  $F_3 F_4 F_2$  contain each a pencil of conics which cannot be taken into consideration so that their planes fall away.

*quadruple points* in  $F_1, F_2$ , *triple points* in  $F_2, F_1$ .  $\mathcal{A}^6$  further contains the straight lines  $g_3, g_4$ , and the *nodal lines*  $s_1, s_2$ ; the latter arises from the observation that  $l$  intersects two curves  $\varrho^3$  meeting  $s_1$  or  $s_2$  in a point  $S_1$  or  $S_2$  lying on them.

The intersection of the surfaces  $\mathcal{A}$  belonging to two straight lines  $l, l'$  consists of: 6 curves  $\varrho^3$ , resting on  $l$  and  $l'$ , the nodal lines  $s_1, s_2, d_{12}$  and the straight lines  $d_{13}, d_{14}, d_{23}, d_{24}, g_3, g_4$ .

The cubic transformation, which, in tetrahedral coordinates is determined by

$$x_1y_1 = x_2y_2 = x_3y_3 = x_4y_4,$$

transforms this congruence into the bilinear congruence of rays, which has the images  $s_1^*, s_2^*$ , of  $s_1, s_2$  as directrices<sup>1)</sup>. The surface  $\mathcal{A}$  passes in consequence of this into the ruled surface formed by the straight lines  $r$ , which rest on  $s_1^*, s_2^*$  and on the curve  $\lambda^3$  passing through the four points  $F'$  into which  $l$  is transformed. The image of  $\mathcal{A}$  is apparently a ruled surface of order four with nodal lines  $s_1^*, s_2^*$ . As this, apart from the points  $F'$ , has six points in common with an arbitrary curve  $\varrho^3$  laid through those points, it is found once more that  $\mathcal{A}$  must be of order six.

Now that the surface  $\mathcal{A}$  is completely known, the characteristic numbers of the congruence may be found in the usual way<sup>2)</sup>.

In an arbitrary plane  $\Phi$  this congruence determines a cubic involution possessing three singular points of order two (the intersections of  $d_{12}, s_1, s_2$ ) and six singular points of order one (the intersections of  $d_{13}, d_{14}, d_{23}, d_{24}, g_3, g_4$ ). It has been more fully described in my paper on "Cubic involutions in the plane".<sup>3)</sup>

**3.** Let us now consider the congruence  $[\varrho^3]$ , which possesses *three fundamental points*  $F_1, F_2, F_3$  and *four singular bisecants*  $s_1, s_1', s_2, s_2'$ , of which the first two pass through  $F_1$ , the other two through  $F_2$ . Here too two pencils of quadratic cones that can produce it are easily pointed out, while the four straight lines  $s$  are again *singular straight lines of order two*.

The degenerate figures  $(d, \sigma^2)$  now form the following groups:

A. The conic  $\sigma^2$  passes through  $F_3$  and rests on the five straight lines  $d_{12} \equiv F_1, F_2, s_1, s_1', s_2, s_2'$ ; the locus of  $\sigma^2$  is the *ruled cubic surface*  $\Delta^3$ , of which  $d_{12}$  is the nodal line, the second transversal  $t$

<sup>1)</sup> This transformation may effectively be used in the investigation of REYE'S congruence (see my paper in volume XI of these Proceedings, p. 84).

<sup>2)</sup> Cf. my paper in vol. XIV (p. 255) of these Proceedings.

<sup>3)</sup> These Proc. XVI, p 974 (§ 6).

of the lines  $s$  being the second directrix. It is quite determined by the lines  $s$  and the transversal out of  $F'_3$  via  $d_{12}$  and  $t$ .

B. In the plane  $(s_2, s_2')$  lies a pencil ( $\sigma^2$ ), having  $F'_2$  and the intersections of  $s_1, s_1'$  and  $d_{13}$  as base-points. Each of these  $\sigma^2$  forms with  $d_{13}$  a figure  $\varrho^3$ .

In the same way  $d_{23}$  is to be combined with a  $\sigma^2$  of a pencil lying in the plane  $(s_1, s_1')$ .

C. The straight line  $t$  may be coupled to any conic  $\sigma^2$  passing through  $F'_1, F'_2, F'_3$ , which meets  $t$ .

D. In the plane  $(F'_3s_1)$  lies a ( $\sigma^2$ ), having as base-points  $F'_1, F'_2$  and the intersections of  $s_2, s_2'$ . The corresponding straight line  $d$  passes through  $F'_2$  and rests on  $s_1'$ . Both component parts of  $(d, \sigma^2)$  are variable.

In the same way each of the planes  $(F'_3s_1'), (F'_3s_2), (F'_3s_2')$  contains a pencil ( $\sigma^2$ ); the corresponding pencils of rays lie in the planes  $(F'_1s_1), (F'_1s_2'), (F'_1s_2)$ .

Here too the figures  $\sigma^2$  form a locus of order ten.

The intersection of the plane  $F'_1F'_2F'_3$  with the surface  $\mathcal{A}$  now consists of a conic (resting on  $l$ ), the straight lines  $F'_1F'_3$  and  $F'_2F'_3$  (belonging to figures  $\sigma^2$ , intersecting  $l$  elsewhere) and the straight line  $F'_1F'_2$ , which is a triple one, because  $\Delta^3$  contains three  $\sigma^2$  resting on  $l$ . The straight line  $l$  consequently determines a surface  $\mathcal{A}'$ , which has  $d_{12}$  as *triple straight line*, passes through  $d_{13}, d_{23}, l$  and possesses *four nodal lines*  $s_1, s_1', s_2, s_2'$ ;  $F'_1, F'_2$  are *quintuple points*,  $F'_3$  is a *triple point*.

In an arbitrary plane  $\Phi$  this congruence determines a cubic involution with *one* singular point of order three, *four* singular points of order two, and *three* singular points of order one.<sup>1)</sup>

4. We shall finally consider the  $[\varrho^3]$ , which has  $F'_1, F'_2$  as *fundamental points*, the straight lines  $s_1, s_1', s_1''$  and  $s_2, s_2', s_2''$  as *singular bisecants*; the first three meet in  $F'_1$ , the other three in  $F'_2$ .

The straight line  $d_{12} \equiv F'_1F'_2$  is triple directrix of a *ruled quartic surface*  $\Delta^4$ , which has the six straight lines  $s$  as generators. Any plane passing through two generators intersecting on  $d_{12}$  intersects  $\Delta^4$  moreover along a conic  $\sigma^2$  resting on  $d_{12}$  and on the straight lines  $s$ , consequently forms a degenerate figure  $\varrho^3$ .

In the plane  $(s_1s_1')$  lies a pencil ( $\sigma^2$ ) having as base-points  $F'_1$  and the intersections of  $s_2, s_2', s_2''$ ; each of these curves forms a figure  $\varrho^3$  with a definite ray  $d$  of the plane pencil which has  $F'_2$  as vertex

<sup>1)</sup> It has been treated more fully in my paper quoted above (Proc. XVI, § 13).

and lies in the plane ( $F_2s_1''$ ). Both component parts are variable.

There are apparently five more systems equivalent to this, each determined by a pencil ( $\sigma^2$ ) and a pencil ( $d$ ).

The locus of the conics  $\sigma^2$  is therefore also here of order ten.

The surface  $A$  appears to be of order eight; it has  $d_{12}$  as *quadruple straight line*, each of the six straight lines  $s$  as *nodal lines*. For if the complete intersection of two surfaces  $A$  is considered, it appears that the order  $x$  is to be found from the equation  $x^2 - 3x - 40 = 0$ ; hence  $x = 8$ .

In a plane  $\Phi$  a cubic involution possessing one singular point of order four and six singular points of order two is determined by this [ $\sigma^3$ ]. It has been described in § 14 of my paper quoted above.

**Chemistry.** — “*Equilibria in Ternary Systems*” XVIII. By Prof. SCHREINEMAKERS.

In the previous communications here and there some equilibria between solid substances and vapour have been brought in discussion already; now we will consider some of these equilibria more in detail. We may distinguish several cases according as  $F$  and  $G$  are unary, binary or ternary phases.

I. The equilibrium  $F + G$ ;  $F$  is a ternary compound,  $G$  a ternary vapour.

The equilibrium  $F + G$  is monovariant ( $P$  and  $T$  constant), this means that the vapours, which can be in equilibrium with solid  $F$ , are represented by a curve. In order to find this curve we construct a cone, which touches the vapourleaf of the  $\zeta$ -surface and which has its top in the point, representing the  $\zeta$  of the solid substance  $F$ . The projection of the tangent curve is the curve sought for, viz. the saturationcurve ( $P$  and  $T$  constant) of the substance  $F$ . From this deduction it is apparent also, that this curve is circumphased and that we cannot construct from  $F$  a tangent to it.

The equilibrium  $F + G$  is determined by:

$$Z_1 + (a-x_1) \frac{\partial Z_1}{\partial x_1} + (\beta-y_1) \frac{\partial Z_1}{\partial y_1} = \zeta \quad \dots \quad (1)$$

When we keep  $P$  and  $T$  constant in (1), it determines the vapour-saturationcurve ( $P, T$ ) of  $F$ . When we assume that in the vapour the compound  $F$  is completely decomposed into its components and that the gas-laws are true, (1) passes into:

$$a \log x_1 + \beta \log y_1 + (1-a-\beta) \log (1-x_1-y_1) = C \quad \dots \quad (2)$$

or :

$$x_1^\alpha y_1^\beta (1-x_1-y_1)^{1-\alpha-\beta} = C_1 \dots \dots \dots (2a)$$

wherein  $C$  and  $C_1$  are independent of  $P$  and  $T$ . When we introduce the partial vapour-tension :

$$P_A = x_1 P, \quad P_B = y_1 P \quad \text{and} \quad P_C = (1-x_1-y_1) P$$

then (2) passes into :

$$\alpha \log P_A + \beta \log P_B + (1-\alpha-\beta) \log P_C = C \dots \dots \dots (3)$$

or :

$$P_A^\alpha \cdot P_B^\beta P_C^{1-\alpha-\beta} = C_1 \dots \dots \dots (3a)$$

When we keep the temperature constant, it follows from (1)

$$\left. \begin{aligned} [(x_1-\alpha) r_1 + (y_1-\beta) s_1] dx_1 + [(x_1-\alpha) s_1 + (y_1-\beta) t_1] dy_1 = \\ = \left[ V_1 - v + (x_1-\alpha) \frac{\partial V_1}{\partial x_1} + (y_1-\beta) \frac{\partial V_1}{\partial y_1} \right] dP \end{aligned} \right\} \dots \dots (4)$$

We call  $l$  the distance from  $F$  to a point  $(x_1, y_1)$  of the vapour-saturationcurve; we take  $dl$  positive in such a direction that  $l$  becomes larger. Then we have :

$$\frac{dl}{l} = \frac{dx_1}{x_1-\alpha} = \frac{dy_1}{y_1-\beta}$$

When we substitute these values of  $dx_1$  and  $dy_1$  in (4) and when we represent the coefficient of  $dP$  by  $\Delta V_1$ , we find :

$$dl = \frac{l \cdot \Delta V_1 \cdot dP}{(x_1-\alpha)^2 r_1 + 2(x_1-\alpha)(y_1-\beta) s_1 + (y_1-\beta)^2 t_1} \dots \dots (5)$$

Herein  $\Delta V_1$  is the increase of volume when 1 mol. solid  $F$  sublimates into such a large quantity of vapour that the composition does not change. It follows from (5) : each point of the vapoursaturationcurve moves on increase of pressure ( $dP > 0$ ) away from  $F$  ( $dl > 0$ ) and on decrease of pressure ( $dP < 0$ ) towards  $F$  ( $dl < 0$ ). We may express this also in the following way : on increase of pressure the vapoursaturationcurve extends itself, on decrease of pressure it contracts.

In a similar way we find : on increase of pressure the vapour-saturationcurve contracts, on decrease of pressure it extends.

When we keep the temperature constant and when we lower the pressure, then the vapoursaturationcurve shall, as it contracts, reduce itself under a definite pressure to the point  $F$ . The solid substance  $F$  is then in equilibrium with a vapour of the composition  $F'$  or in other words : the solid substance  $F$  sublimates. To every temperature  $T$  consequently a definite pressure  $P$  belongs, under which  $F$  sublimates. When we draw in a  $P, T$ -diagram the temperatures and the

corresponding sublimation-pressures, we obtain the sublimationcurve of the substance  $F$ . [Confer for instance curve  $aK$  in fig. 3 (III)]. Previously we saw that this curve ends in the uppermost sublimationpoint  $K$ ; at higher temperatures viz. is formed solid  $F$  + liquid + vapour. When the formation of liquid fails to make its appearance, this curve may be extended of course.

II. The equilibrium  $F + G$ ;  $F$  is a binary compound,  $G$  is a ternary vapour.

With the aid of the vapourleaf of the  $\zeta$ -surface we find that the vapours, which can be in equilibrium with solid  $F$ , form again a curve. When  $F$  is a binary compound of  $B$  and  $C$ , this vapoursaturationcurve has two terminatingpoints on side  $BC$ ; the point  $F$  is always situated between these two terminatingpoints. Therefore we call this curve circumphased again. Consequently the binary compound can be in equilibrium with a series of ternary vapours and with two binary vapours, consisting of  $B$  and  $C$ . The equilibrium is determined by (1) when we put herein  $a = 0$ . We find from this for the vapoursaturationcurve:

$$[x_1 r_1 + (y_1 - \beta) s_1] dx_1 + [x_1 s_1 + (y_1 - \beta) t_1] dy_1 = 0 \quad . \quad (6)$$

[We find this also from (4) by putting herein  $a = 0$  and  $dP = 0$ ]. For a terminatingpoint of this curve on the side  $BC$  is  $x_1 = 0$  and  $\text{Lim } x_1 r_1 = RT$ ; the tangent in this terminatingpoint is consequently fixed by:

$$\left( \frac{dy_1}{dx_1} \right)_{x_1=0} = - \frac{RT + (y_1 - \beta) s_1}{(y_1 - \beta) t_1} = - \frac{y_1 (1 - y_1) + y_1 - \beta}{y_1 - \beta} \quad . \quad (7)$$

The first expression is generally applicable; the second only when the gas-laws hold good.

The rules mentioned sub I apply to the movement of this curve on change of  $P$  or of  $T$ .

In a similar way as we have acted in I, we find also here, that at each temperature a definite pressure exists, under which the vapoursaturationcurve reduces itself to the point  $F$ ; this pressure is the sublimation-pressure of the binary compound  $F$ . Therefore we may draw in a  $P, T$ -diagram a sublimationcurve of  $F$ .

III. The equilibrium  $F + G$ ;  $F$  is one of the components,  $G$  is a ternary vapour.

We find that the vapours, being in equilibrium with solid  $F$ , form again a curve. When  $F$  is the component  $B$ , this vapoursaturationcurve has two terminatingpoints, the one on side  $BA$ , the other on side  $BC$ . The component  $B$  can, therefore, be in equilibrium with

a series of ternary and with two binary vapours. The one binary vapour contains  $B$  and  $C$ , the other  $B$  and  $A$ . The equilibrium is determined by (1) when we put herein  $\alpha = 0$  and  $\beta = 0$ . The rules mentioned above, apply again to the movement of this curve on change of  $P$  or of  $T$ . The same as in the case I applies to the disappearance of the vapour saturation curve in point  $B$ , to the sublimation-pressure and to the sublimation curve of  $B$ .

IV. The equilibrium  $F + F' + G$ ;  $G$  is a ternary vapour.

We distinguish herewith two cases, according as the solid substances together contain the three components or not.

1.  $F$  and  $F'$  contain together the three components.

The line  $FF'$  consequently is situated within the triangle; of course this is always the case, when one of the substances or both are ternary compounds. It may however be also the case when both substances are binary compounds and even when one of those is one of the components.

The equilibrium  $F + F' + G$  is, under a constant  $P$  and at a constant  $T$ , invariant; this means that at a given temperature and under a given pressure the vapour has a fixed composition. We may understand this also in the following way. We imagine under the given  $P$  and at the given  $T$  the vapour saturation curves of  $F$  and  $F'$  to be drawn. These may either intersect one another or not; they can touch one another as transition-case. When they do not intersect one another, no vapours exist; when they intersect one another, two vapours  $G_1$  and  $G_2$  exist, which may be in equilibrium with  $F + F'$ , both these vapours are situated on the two sides of the line  $FF'$ . The points  $F, F'$  and  $r$  may be situated with respect to one another in three ways.

A. The point  $r$  is situated between  $F$  and  $F'$ ; consequently the two curves touch one another outwardly in  $r$ . Consequently the reaction  $F + F' \rightleftharpoons G$  may occur. When we bring  $F$  and  $F'$  into a space, a part of each of these substances evaporates in order to form the vapour  $G$ . We call this a congruent sublimation of  $F + F'$ .

B. The point  $F'$  is situated between  $F$  and  $r$ ; both the curves touch one another in  $r$ , consequently externally; the vapour saturation curve of  $F$  surrounds that of  $F'$ . Consequently the reaction  $F' \rightleftharpoons F + G$  may occur. When we bring  $F$  and  $F'$  into a space, then, in order to form the vapour  $G$ , only a part of  $F'$  shall evaporate, while at the same time solid  $F$  is separated. In order to obtain the equilibrium  $F + F' + G$ , consequently we have only to

bring a sufficient quantity of  $F$  into a space. We call this an incongruent sublimation of  $F + F'$ .

*C.* The point  $F$  is situated between  $F'$  and  $r$ . This case is exactly analogous with the previous.

*D.* As transitioncase between  $A$  and  $B$  (or  $C$ ) point  $r$  coincides with  $F'$  (or  $F$ ). We shall refer to this later.

When we lower the pressure below  $P_r$ , the points of intersection disappear. In the case, mentioned sub  $A$ , then the two curves are situated outside one another; the equilibria  $F + G$  and  $F' + G$  then both occur in stable condition. On further decrease of  $P$  these curves disappear; that of  $F$  under the sublimationpressure of  $F$ , that of  $F'$  at the sublimationpressure of  $F'$ .

In the case  $B$  the two curves touch one another internally in  $r$ ; further the curve of  $F'$  is surrounded by that of  $F$ . On decrease of  $P$  both the curves contract and then two cases are imaginable. When in the vicinity of  $r$  curve  $F$  contracts more rapidly than curve  $F'$ , two points of intersection arise; when, however, curve  $F'$  contracts more rapidly than curve  $F$ , curve  $F'$  happens to fall completely within curve  $F$ . In order to show that only this latter is the case, we apply (5) to the point of contact  $r$  of the two curves. When we represent  $Fr$  by  $l$ , formula (5) is true for curve  $F$ . When we represent  $F'r$  by  $l'$ , then for curve  $F'$  a formula (5) is true, in which  $l$ ,  $\alpha$  and  $\beta$  are replaced by  $l'$ ,  $\alpha'$  and  $\beta'$ . As the value of  $\Delta V_1$  is very approximately the same in both the formulae, the relation  $dl : dl' = l' : l$  follows. This means: on change of  $P$  the velocities of the two curves in the vicinity of their point of contact are in inverse ratio to one another, as the distances from  $r$  to  $F$  and  $F'$ . In the case, now under consideration, ( $l > l'$ ) curve  $F'$  consequently moves in the vicinity of the point  $r$  more rapidly than curve  $F$ . On increase of  $P$  consequently two points of intersection arise; on decrease of  $P$  these points of intersection disappear and curve  $F'$  is completely surrounded by curve  $F$ . The equilibrium  $F + G$  occurs, therefore, in stable condition; the equilibrium  $F' + G$  can occur only in metastable condition.

When we lower the pressure still further, firstly curve  $F'$  disappears and afterwards curve  $F$ ; consequently the sublimation-point of the substance  $F'$  is metastable. In the case  $A$ ,  $F$  and  $F'$  may both sublime without decomposition; in the case  $B$  only  $F$  sublimes without decomposition, while  $F'$  converts itself into  $F + G$ .

As to the case  $B$  analogous considerations apply to the case  $C$ .

From the previous considerations among others the following can be deduced: To each temperature  $T$  belongs a definite congruent or

incongruent sublimationpressure of  $F + F'$ . This sublimationpressure is higher than that of each of the substances  $F$  and  $F'$  separately, independent of whether both or only one of them has a stable sublimationpressure.

When we draw in a  $P, T$ -diagram the temperatures and the corresponding sublimationpressures of  $F$ ,  $F'$  and  $F + F'$ , we obtain three curves. In fig. 1 (VII)  $aK$  is the sublimationcurve of  $F$ ,  $a'K'$  that of  $F'$  and  $a''D$  that of  $F + F'$ . According to the previous curve  $a''D$  must of course be situated higher than the curves  $aK$  and  $a'K'$ . Formerly we saw that these curves terminate in  $K$ ,  $K'$  and  $D$ ; when the formation of liquid fails to come, we can pursue them further.

In the case  $A$  the curves  $aK$ ,  $a'K'$  and  $a''D$  can be realised in stable condition; for this we must bring into a space solid  $F$ , or  $F'$  or  $F + F'$  and we must take care that the solid substances are not evaporated completely. In fig. 1 (VII)  $a'K'$  is situated above  $aK$ , the reverse can of course be the case also.

In the case  $B$  only the curves  $aK$  and  $a''D$  may be realised in stable condition, for this purpose we must bring into a vacuum  $F$  or  $F + F'$ . When, however, we bring  $F'$  into a space, then solid  $F' +$  vapour  $F'$  is not formed, but in more stable condition  $F + F' +$  vapour. Consequently we do not determine the sublimationcurve  $a'K'$  of  $F'$ , but that of  $F + F'$ , therefore, curve  $a''D$ . We would be able to determine the curve  $a'K'$ , only when the reaction  $F' \rightarrow F + G$  failed to come. Further it is apparent that curve  $a'K'$  must be situated higher than  $aK$ .

Analogueous considerations apply to the case  $C$  as in the preceding case  $B$ .

In the transition case  $D$  we assume that  $r$  coincides with  $F$ . While the cases  $A$ ,  $B$ , and  $C$  may occur at a series of temperatures,  $D$  occurs at a definite temperature only. In order to understand this, we imagine the vapoursaturationcurves of  $F$  and  $F'$ , which touch one another in a point  $r$  on the line  $FF'$ . When we change the temperature, we must also change the pressure, in order to let the two curves touch one another again; their point of contact  $r$  however, shall also get another place on the line  $FF'$ . Consequently on change of  $T$  not only the sublimation-pressure of  $F + F'$ , but also the composition of the vapour  $r$  changes. As, therefore, the point  $r$  shifts on change of temperature along the line  $FF'$ , it may coincide at a definite temperature with  $F'$ . The vapoursaturation-curve of  $F'$  is reduced in this case to the point  $F'$  and that of  $F$  goes through the point  $F'$ . The pressure corresponding with this

temperature is consequently the sublimation-pressure of  $F'$ . Therefore we find:  $r$  can coincide with  $F'$ ; the equilibrium  $F + F' + G$  passes then into  $F + F' + \text{vapour } F'$ . This can only be the case at a definite temperature and under a corresponding pressure; this pressure is the sublimation-pressure of  $F'$ .

In the  $P, T$ -diagram the sublimation-curves of  $F + F'$  and of  $F'$  have, therefore, a point in common with one another, as the first curve is situated generally above the second, the two curves touch consequently one another in this point. We may express this also in the following way: when in the concentration-diagram the common point of contact of two vapour-saturation-curves goes through  $F'$ , then in the  $P, T$ -diagram the sublimation-curves of  $F + F'$  and  $F'$  touch one another.

This point of contact divides both the curves into two parts. At the one side of this point on the curve of  $F + F'$  congruent sublimation takes place and the curve of  $F'$  is stable; at the other side of this point on the curve of  $F + F'$  incongruent sublimation takes place and the curve of  $F'$  is metastable.

2.  $F$  and  $F'$  contain together two components only.

The line  $FF'$  coincides, therefore, with one side of the triangle. This is always the case when both the substances are components; it may yet also be the case when one of them or both substances are binary compounds. The previous considerations sub IV. 1. apply still also now, with slight changes however, which we shall indicate briefly. Firstly we take (at  $T$  constant) a pressure, under which the two vapour-saturation-curves intersect one another. The two curves have, however, one point of intersection now, so that only one equilibrium  $F + F' + G$  occurs. When we assume, for fixing the ideas, that  $F$  and  $F'$  contain together the components  $B$  and  $C$ , this point of intersection moves on decrease of pressure towards the side  $BC$ , in order to fall on the side  $BC$  under a definite pressure  $P_r$ . As  $r$  is now a binary vapour, the equilibrium  $F + F' + G_r$  is binary;  $P_r$  is the sublimation-pressure of  $F + F'$ .

Although  $F$ ,  $F'$  and  $r$  are situated on a straight line, yet the two curves do not touch one another in this point  $r$  in this case; this is, as we have seen above, indeed the case when  $r$  is situated within the triangle. The cases  $A$ ,  $B$  and  $C$  of IV. 1. apply to the position of the points  $F$ ,  $F'$  and  $r$  with respect to one another.

On further decrease of pressure the two curves contract, the same as is described in IV. 1 applies to their position with respect to one another, the considerations given there about the sublimation-curves remain also valid here.

It follows immediately from the direction of the tangent which is determined by (7) that, as has been said above, the two curves do not touch one another in the point  $r$  on side  $BC$ . As this direction depends not only on  $\gamma_1$ , but also on  $\beta$ , and as  $\beta$  is different for  $F$  and  $F'$ , the two tangents do not coincide.

V. The equilibrium  $F + F' + F'' + G$ ;  $G$  is a ternary vapour.

We may also distinguish here two cases, according as the solid substances contain together the three components or not.

1.  $F$ ,  $F'$  and  $F''$  are not situated on a straight line.

As the three components occur in four phases, the equilibrium is monovariant, consequently at each temperature it exists under a definite  $P$  only and also the vapour has a definite composition. We can understand this also in the following way. We imagine the vapour saturationcurves of  $F$ ,  $F'$  and  $F''$  to be drawn for any  $T$  and  $P$ ; it is evident that as a maximum six points of intersection can occur. Now we change the pressure, while the temperature remains constant; a definite pressure  $P_u$  will occur, under which the three curves go through one and the same point  $u$ . Consequently the equilibrium  $F + F' + F'' + G$  occurs under a definite pressure  $P_u$  and the vapour  $G$  has then the composition  $u$ . As each curve intersects each of the two other curves in two points,  $P_u$  is higher than the sublimationpressure of the three pairs of liquids:  $F + F'$ ,  $F + F''$  and  $F' + F''$ . Consequently we find: the sublimationpressure of  $F + F' + F''$  is larger than that of  $F + F'$ ,  $F + F''$  and  $F' + F''$  and, therefore, also larger than that of  $F$ ,  $F'$ , and  $F''$ .

Now we can distinguish three cases, according to the position of  $u$  with respect to the solid substances.

A. The reaction  $F + F' + F'' \rightleftharpoons G$  occurs. When we bring, therefore, the three substances into a space, a part of each of these substances evaporates in order to form the vapour  $G$ . Consequently we have a congruent sublimation of  $F + F' + F''$ .

B. The reaction  $F + F' \rightleftharpoons F'' + G$  occurs. When we bring  $F$ ,  $F'$  and  $F''$  into a space, consequently, in order to form  $G$ , only a part of  $F$  and  $F'$  will evaporate, while at the same time solid  $F''$  is deposited. In order to obtain the equilibrium  $F + F' + F'' + G$ , we have, therefore, only to bring a sufficient quantity of  $F + F'$  into a space. Consequently we have an incongruent sublimation of  $F + F' + F''$ .

C. The reaction  $F \rightleftharpoons F' + F'' + G$  occurs. When we bring the three solid substances into a space, then, in order to form the vapour  $G$ , only a part of  $F$  will evaporate, while at the same

time solid  $F' + F''$  is deposited. In order to obtain the equilibrium  $F + F' + F'' + G$ , consequently we have only to bring a sufficient quantity of  $F$  into a space. We have, therefore, again a congruent sublimation.

D. The vapour  $G$  is represented by a point, which is situated with two of the solid substances on a straight line. We shall refer to this later.

When we change the temperature, then also the sublimation-pressure of  $F + F' + F''$  changes, consequently in a  $P, T$ -diagram a sublimationcurve of  $F + F' + F''$  may be drawn. Herein the sublimationcurve of  $F + F' + F''$  is situated higher than that of  $F + F'$ ,  $F + F''$  and  $F' + F''$ , that of  $F + F'$  higher than that of  $F$  and  $F'$ , that of  $F + F''$  higher than that of  $F$  and  $F''$  and that of  $F' + F''$  higher than that of  $F'$  and  $F''$ . Of these seven curves, several may represent metastable conditions. To each of these sublimationcurves applies:

$$T \frac{dP}{dT} = \frac{\Delta W}{\Delta V} \cdot \dots \dots \dots (8)$$

Herein  $\Delta W$  is the heat, which must be added,  $\Delta V$  the change of volume, when a reaction occurs under a constant  $P$  and at a constant  $T$  between the phases, which are in equilibrium. When the gas-laws are valid (8) can also be written in another form.

We can represent the sublimationcurve of  $F + F' + F''$  also in the concentration-diagram. At change of  $T$  we change viz. not only the sublimationpressure, but also the composition of the vapour  $G$  (point  $u$ ). The point  $u$  consequently traces a curve in the concentration diagram, the sublimationcurve of  $F + F' + F''$ . With each point of this curve a definite  $T$  and  $P$  correspond.

When this curve intersects one of the sides (or its prolongation) of the threephase-triangle  $FF'F''$ , the transitioncase mentioned sub  $D$  occurs. We assume that this point of intersection  $u$  is situated on the line  $FF'$ . Consequently a definite temperature  $T_u$  and a definite pressure  $P_u$  belong to this point  $u$ . When we imagine the vapoursaturation-curves of  $F$ ,  $F'$  and  $F''$  to be drawn, it is apparent that those of  $F$  and  $F'$  touch one another in the point  $u$ . Consequently the pressure  $P_u$  is the congruent or incongruent sublimation-pressure of  $F + F'$  belonging to the temperature  $T_u$ . In the  $P, T$ -diagram the sublimation-curves of  $F + F' + F''$  and  $F + F'$  will therefore, touch one another at the temperature  $T_u$ . Consequently we find: when in the concentration-diagram the sublimationcurve of  $F + F' + F''$  intersects the line  $FF'$ , then in the  $P, T$ -diagram the sublimationcurves of  $F + F' + F''$  and  $F + F'$  touch one another in the  $P, T$ -diagram.

We may also imagine the case that the sublimationcurve of  $F + F' + F''$  goes casually through the point  $F'$ . We see easily that then in the  $P, T$ -diagram the sublimationcurves of  $F + F' + F''$ ,  $F + F'$ ,  $F + F''$  and  $F$  touch one another.

The sublimationcurve of  $F + F' + F''$  ends when a new phase  $X$  occurs;  $X$  can be a solid substance or a liquid. This equilibrium  $F + F' + F'' + X + G$  is invariant; it exists, therefore, only at a definite  $T$  and under a definite  $P$ . In the  $P, T$ -diagram it is consequently represented by a point, the quintuple point. Five quadruplecurves proceed from this quintuplepoint, the position of these curves and of the threephase regions with respect to one another is fixed by definite rules and is dependent on the position of the five phases in the concentration-diagram. <sup>1)</sup>

2.  $F, F'$  and  $F''$  are situated in a straight line.

We distinguish, with respect to the position of this line  $FF'F''$  two cases.

A. The substances together contain the three components, the line  $FF'F''$  is, therefore, situated within the components-triangle. In order to find the vapour, which is in equilibrium with  $F + F' + F''$ , we may act in the following way. We represent the  $\zeta$ 's of the solid substances  $F, F'$  and  $F''$  by  $F_1, F_1'$  and  $F_1''$ . As  $F, F'$  and  $F''$  are situated on a straight line,  $F_1, F_1'$  and  $F_1''$  are situated in a vertical plane, but generally not on a straight line. Consequently the equilibrium  $F + F' + F''$  cannot occur and of the equilibria  $F + F', F + F''$  and  $F' + F''$  two (one) are stable and, therefore, one (two) are metastable. Now we take a definite  $P$  and  $T$ ; we keep the temperature constant and we change the pressure; under a definite pressure the points  $F_1, F_1'$  and  $F_1''$  fall then in a straight line, so that the equilibrium  $F + F' + F''$  occurs.

When this line is situated below the vapourleaf of the  $\zeta$ -surface, then the equilibrium  $F + F' + F''$  is stable; we can construct then through this line two tangentialplanes to the vapourleaf; we call  $u$  and  $v$  the projections of the two points of contact. These points  $u$  and  $v$  are situated on either side of the line  $FF'F''$ . At the assumed temperature consequently a pressure  $P_u = P_v$  exists, under which occur the equilibria:  $F + F' + F''$ ,  $F + F' + F'' + G_u$  and  $F + F' + F'' + G_v$ .

Generally the vapoursaturationcurves of  $F, F'$  and  $F''$  intersect one another in six points; it is apparent from the previous that

<sup>1)</sup> F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von BAKHUIS ROOZEBOOM, III, 218—248.

they intersect one another under the pressure  $P_u = P_v$  only in two points, viz.  $u$  and  $v$ . It follows from the intersection of these curves that the pressure  $P_u = P_v$  is greater than the sublimation pressure of  $F + F'$ ,  $F + F''$  and  $F' + F''$ .

We have seen above that at each temperature a pressure  $P_u = P_v$  exists, under which the points  $F_1$ ,  $F'_1$  and  $F''_1$ , fall in a straight line. When this line is situated below the vapourleaf of the  $\zeta$ -surface, the equilibria:  $F + F' + F''$ ,  $F + F' + F'' + G_u$  and  $F + F' + F'' + G_v$  occur in stable condition. When this line is situated above the vapourleaf or when it intersects the vapourleaf, then the equilibrium  $F + F' + F''$  is metastable and the equilibria  $F + F' + F'' + G$  are impossible. As transition-case this line touches the vapourleaf at a definite temperature  $T_r$  and under a corresponding pressure  $P_r$ ; the projection  $r$  of the point of contact is situated on the line  $FF'F''$ . The vapour saturation curves of  $F$ ,  $F'$  and  $F''$  touch one another at this temperature and under this pressure consequently in the point  $r$ . In this transition case the vapour pressure is  $P_r$ , therefore, not larger but equal to the sublimation pressure of  $F + F'$ ,  $F + F''$  and  $F' + F''$ .

When we bring the three substances at a given temperature into a space, then vapour is formed, the composition of which is represented by a point of the line  $FF'F''$ . It is apparent from this that the equilibrium  $F + F' + F'' + G_u$  (or  $G_v$ ) cannot arise in this way, unless casually the temperature  $T_r$  was chosen. Therefore, we shall not call the pressure  $P_u = P_v$  the sublimation pressure, but the equilibrium pressure of  $F + F' + F''$ . When we bring together the three solid phases into a space, generally, therefore, one of them will disappear; then one of the equilibria  $F + F' + G$ ,  $F + F'' + G$  or  $F' + F'' + G$  is formed. Then the pressure becomes also not the equilibrium pressure  $P_u = P_v$ , but one of the lower sublimation pressures.

We may draw the equilibrium  $F + F' + F'' + G$  as well in the  $P, T$ , as in the concentration diagram. When we draw the compositions of the vapours  $G_u$  and  $G_v$  in the concentration diagram, the points  $u$  and  $v$  trace a curve on change of  $T$ . Definite  $T$  and  $P$  correspond with each point of this curve. At the temperature  $T_r$  the points  $u$  and  $v$  coincide in the point  $r$  of the line  $FF'F''$ . This point  $r$  divides the curve into two parts; with each point  $u$  of the one branch viz. a point  $v$  of the other branch corresponds and in this way, that a same  $T$  and  $P$  belong to these points. Hence it follows that along this curve in the point  $r$ ,  $T$  and  $P$  (consequently  $T_r$  and  $P_r$ ) are maximum or minimum.

In order to examine this more in detail, we take the conditions of equilibrium for  $F + F' + F'' + G$ ; they are:

$$Z_1 + (\alpha - x_1) \frac{\partial Z_1}{\partial x_1} + (\beta - y_1) \frac{\partial Z_1}{\partial y_1} - \zeta = 0. \quad (9)$$

and still two of such equations wherein the magnitudes, which relate to the solid substance  $F$ , have been replaced by those of  $F'$  and  $F''$ . With the aid of (9) we may write them also in this way:

$$(\alpha - \alpha') \frac{\partial Z_1}{\partial x_1} + (\beta - \beta') \frac{\partial Z_1}{\partial y_1} + \zeta' - \zeta = 0 \quad (10)$$

and

$$(\alpha - \alpha'') \frac{\partial Z_1}{\partial x_1} + (\beta - \beta'') \frac{\partial Z_1}{\partial y_1} + \zeta'' - \zeta = 0 \quad (11)$$

The conditions (9), (10) and (11) are generally valid, when  $F$ ,  $F'$  and  $F''$  are situated on a straight line, we have

$$(\beta - \beta') : (\alpha - \alpha') = (\beta - \beta'') : (\alpha - \alpha'') = \mu \quad (12)$$

It follows from (10) and (11) with the aid of (12) that:

$$(\alpha'' - \alpha') \zeta + (\alpha - \alpha'') \zeta' + (\alpha' - \alpha) \zeta'' = 0. \quad (13)$$

This equation (13) is at the same time the condition for the occurrence of the equilibrium  $F + F' + F''$ . It is apparent from this, therefore, as has already been found above, that the equilibria  $F + F' + F''$  and  $F + F' + F'' + G$  occur at the same  $T$  and under the same  $P$ . From (13) follows:

$$\frac{dH}{dT} = \frac{(\alpha'' - \alpha')\eta_1 + (\alpha - \alpha'')\eta_1' + (\alpha' - \alpha)\eta_1''}{(\alpha'' - \alpha')v + (\alpha - \alpha'')v' + (\alpha' - \alpha)v''} = \frac{\Delta H}{\Delta V} = \frac{\Delta W}{T\Delta V} \quad (14)$$

which is true as well for the equilibrium  $F + F' + F''$  as for  $F + F' + F'' + G$ . The meaning of  $\Delta H$ ,  $\Delta W$  and  $\Delta V$  is easily seen. When we choose the reaction in such a way that  $\Delta W$  is positive, then  $\Delta V$  may be  $\geq 0$ . The equilibrium  $F + F' + F'' + G$  is fixed by (9), (10) and (14). Now we shall consider it in the point  $r$ : the point of intersection of the equilibrium-curve with the line  $F'F''$ . In this point:

$$(\beta - \beta') : (\alpha - \alpha') = (\beta - y_1) : (\alpha - x_1) = \mu \quad (14)$$

when we develop (9) into a series, we find:

$$\left. \begin{aligned} (r_1 + \mu s_1) dx_1 + (s_1 + \mu t_1) dy_1 + \left( \frac{V_1 - v}{\alpha - x_1} + A \right) dP - \left( \frac{H_1 - \eta_1}{\alpha - x_1} + B \right) dT + \\ + \frac{1}{2} \left( -\frac{r_1}{\alpha - x_1} + C \right) dx_1^2 + \left( -\frac{s_1}{\alpha - x_1} + D \right) dx_1 dy_1 + \\ + \frac{1}{2} \left( -\frac{t_1}{\alpha - x_1} + E \right) dy_1^2 + \frac{R}{\alpha - x_1} = 0. \end{aligned} \right\} \quad (15)$$

It follows from (10) that:

$$\left. \begin{aligned} (r_1 + \mu s_1)dx_1 + (s_1 + \mu t_1)dy_1 + \left(\frac{v'-v}{a-a'} + A\right)dP - \left(\frac{\eta'-\eta}{a-a'} + B\right)dT + \\ + \frac{1}{2}Cdx_1^2 + Ddx_1dy_1 + \frac{1}{2}Edy_1^2 + \frac{R'}{a-a'} = 0 \end{aligned} \right\} \quad (16)$$

We may easily calculate what is represented in (15) and (16) by  $A$ ,  $B$ ,  $C$ ,  $D$  and  $E$ .  $R$  and  $R'$  contain only terms which are infinitely small with respect to those, which have been written down already. When we subtract (15) from (16) and when we put for the sake of abbreviation:

$$\frac{1}{2}r_1dx_1^2 + s_1dx_1dy_1 + \frac{1}{2}t_1dy_1^2 = K \quad . \quad . \quad . \quad (17)$$

then we find:

$$\left(\frac{V_1-v}{a-x_1} - \frac{v'-v}{a-a'}\right)dP - \left(\frac{H_1-\eta}{a-x_1} - \frac{\eta'-\eta}{a-a'}\right)dT - \frac{K}{a-x_1} = R'' \quad (18)$$

Herein  $R''$  contains only terms which are infinitely small with respect to  $dP$ ,  $dT$ ,  $dx_1^2$ ,  $dx_1dy_1$  and  $dy_1^2$ . Now between the phases  $F$ ,  $F'$  and  $G$  we imagine a reaction to take place, at which the unity of quantity of vapour is generated. Let  $\Delta V_1$  be the increase of volume,  $\Delta H$ , the increase of entropy at this reaction. When we put as first approximation in (18)  $R'' = 0$ , then follows:

$$\Delta V_1 \cdot dP - \Delta H_1 \cdot dT = K \quad . \quad . \quad . \quad , \quad . \quad (19)$$

Hence follows with the aid of (14):

$$\left(\Delta V_1 - \frac{\Delta H_1}{\Delta H} \cdot \Delta V\right)dP = K \quad . \quad . \quad . \quad . \quad (20)$$

$\Delta V_1$  is a thousand times larger than  $\Delta V$ ; consequently the coefficient of  $dP$  is generally positive; it is apparent from (17) that  $K$  is also positive. Therefore we find  $dP > 0$  or: the pressure is a minimum in  $r$ . As  $dT = \frac{\Delta V}{\Delta H} \cdot dP$ ,  $dT$  is  $\geq 0$ ; consequently the temperature is in  $r$  maximum or minimum.

Now we consider the  $P, T$ -diagram. The equilibrium  $F + F' + F''$  is represented by a curve; as on this curve the conversion of one of the solid substances takes place into the two others, or reversally, we call this curve the conversion-curve. It follows from (14) that on increase of  $T$  the pressure can as well increase as decrease. The equilibrium-curve  $F + F' + F'' + G$  coincides with the conversion-curve; it covers this curve, however, only partly. As the pressure is a minimum in its terminatingpoint  $r$ , it proceeds starting from  $r$  towards higher pressures. Through this point  $r$  moreover go the

sublimation-curves of  $F + F'$ ,  $F + F''$  and  $F' + F''$ . It is apparent from (8) that these three curves do not touch one another in  $r$ , but they intersect one another. According to our previous considerations, these curves, except in the point  $r$ , are always situated below the equilibrium-curve  $F + F' + F'' + G$ . Further it appears that at the one side of the point  $r$  two of these curves represent stable conditions, on the other side one of these curves.

Consequently we find: in the point  $r$  five curves come together, the conversion-curve ( $F + F' + F''$ ) and the equilibrium-curve ( $F + F' + F'' + G$ ) of which coincide. This last curve ends in  $r$ ; the four other curves go through this point; the point  $r$  divides these curves into two parts, the one of which represents stable conditions and the other metastable conditions.

We find these results also in the following way. We may consider the equilibrium  $F + F' + F'' + G$ , when  $G$  is represented by a point of  $FF'F''$ , consequently it is invariant and it can be represented in the  $P, T$ -diagram by a point  $r$ . Therefore, through  $r$  four triple-curves must go, viz. the conversion-curve ( $F + F' + F''$ ) and the sublimation-curves of  $F + F'$ ,  $F + F''$  and  $F' + F''$ . When we consider stable conditions only, we may say that these curves start all from  $r$  or that they end in  $r$ . The situation of these four curves with respect to one another is fixed by a definite rule.<sup>1)</sup> We may determine the direction of these curves with the aid of the iso-volumetric and the isentropic reaction, which can occur between these 4 phases.<sup>2)</sup> Let the isentropic reaction be:



wherein one or two of the coefficients  $n$ ,  $n'$  and  $n''$  can be negative; in the ordinary manner we must write the phases relating to that in the right part of the equation. As the volume of the vapour  $G$  is very large with respect to that of the solid substances, the reaction will take place from the right to the left with decrease of volume. The equilibria, which are formed at this reaction (from the right to the left) occur consequently under higher pressures. As we, in order to get the equilibrium  $F + F' + F''$ , must cause the reaction to take place from the right to the left, the conversion-curve ( $F + F' + F''$ ) will go consequently always starting from  $r$  towards higher pressures. This is in accordance with our previous considerations,

<sup>1)</sup> F. A. H. SCHREINEMAKERS, Z. f. Phys. Chem. **82** 59 (1913).

F. E. C. SCHEFFER, These Procéedings **21** 446 (1912).

<sup>2)</sup> F. A. H. SCHREINEMAKERS, Die heterogenen Gleichg. von BAKHUIS ROOZEBOM, III<sup>1</sup>, 219—220.

We may also represent the isovolometric reaction by (21), then the coefficients will have another value. As at the reaction from right to left heat can as well be given out as absorbed, the equilibrium  $F + F' + F''$  can, therefore, starting from  $r$  go as well towards higher as towards lower temperatures.

*Leyden, Anorg. Chem. Lab.*

*(To be continued).*

**Chemistry.** — “*Action of Sunlight on the Cinnamic Acids*”. By Dr. A. W. K. DE JONG. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of March 27, 1915).

Some time ago <sup>1)</sup> I communicated that *allo*-cinnamic acid is converted in sunlight into  $\alpha$ -,  $\beta$ -truxillic acid and normal cinnamic acid.

In a communication as to this photo-action in the *Recueil* <sup>2)</sup> I drew, in connexion with the progressive change of the transformation and also because the addition of normal cinnamic to the *allo*-acid increased the quantity of  $\beta$ -truxillic acid, the conclusion that  $\beta$ -truxillic acid was formed by the combination of one molecule of *allo*-acid with one molecule of normal acid.

For a further study of  $\beta$ -truxillic acid it was of great importance to possess larger quantities of the same.

The preparation may take place from the split off coca acids, or from the *allo*-cinnamic acid that has been affected by sunlight.

The first process is tedious and, from a comparatively large quantity of split off acids, it yields but a small amount of  $\beta$ -truxillic acid.

In connexion herewith, attention may be called to the fact that commercial cinnamic acid may often contain not unappreciable quantities of  $\beta$ -truxillic acid which very likely has got into it in the preparation of the cinnamic acid from the above coca acids (both acids possess calcium salts sparingly soluble in water). For instance, a product called *Ac. cinnamylicum puriss. D. Ap. V.* contained 1.8% and another labelled *Ac. cinnamylicum synth. puriss* 3% of  $\beta$ -truxillic acid, whilst in the *Ac. cinnamylicum purum* of the same works occurred a trace. The  $\beta$ -truxillic acid, being the stronger acid, may be readily separated from the cinnamic acid by dilute aqueous sodium hydroxide.

<sup>1)</sup> Proc. **14**, 100 (1911).

<sup>2)</sup> R. **31**, 258 (1912).

The second way of preparing  $\beta$ -truxillic acid did, however, not seem difficult, if only a sufficient quantity of *allocinnamic* acid were at disposal.

Owing to the researches of STOERMER<sup>1)</sup> to whom belongs the credit of having found an easy method for the preparation of the *allo*-form of cinnamic acid and its derivatives, it was possible to prepare the *allo*-acid from cinnamic acid with the aid of sunlight. A solution of sodium cinnamate was exposed daily in large bottles to sunlight and after a few months the *allocinnamic* acid was isolated in the usual manner as the aniline salt. In this manner, I came, in a short time, in possession of a fairly large quantity of *allocinnamic* acid.

As the conditions, in which the most advantageous formation of  $\beta$ -truxillic acid takes place, were not yet known, it was first of all ascertained what influence can be exerted by different factors.

For these experiments I used porcelain dishes. The *allocinnamic* acid was dissolved and by evaporating the liquid and moving the dish thus allowing it to spread all over the sides of the dish, the distribution of the acid over the surface was made as even as possible. The exposure to light took place simultaneously and for the same length of time.

After the end of the exposure the product was treated as follows.

The acids were dissolved in dilute ammonia and this solution was precipitated with barium chloride. After 24 hours the precipitate was collected, washed and the  $\beta$ -truxillic acid liberated by means of hydrochloric acid. The filtrate from the barium salt was acidified with hydrochloric acid, the precipitate collected, washed and dried. By heating with benzine the cinnamic acid was separated from the  $\alpha$ -truxillic acid.

It was found that the fusion of the *allocinnamic* acid (which readily takes place in sunlight) was prejudicial to the formation of  $\beta$ -truxillic acid as it causes the acid to collect in droplets. Hence, in the other experiments the dishes were kept cold by allowing them to float upon water.

The size of the surface over which the acid was distributed also exerted an influence, which will be readily understood, as a small surface receives in the same time less light than a large one.

Also in sunlight, in the same time, more  $\beta$ -truxillic acid was formed than in diffused daylight.

The covering with a glass plate impeded the formation of  $\beta$ -truxillic acid.

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<sup>1)</sup> Ber. **42**, 4865 (1909) **44**, 637 (1911).

The transformation was very much favoured by repeatedly interrupting the illumination and redissolving and recrystallising the mass.

The addition of benzoic acid,  $\alpha$ - or  $\beta$ -truxillic acid to the *allo*-cinnamic acid ( $\frac{1}{2}$  gram *allo*acid + 1 gram of the other acids) was found to be injurious, whereas the admixture with cinnamic acid was very advantageous. From half a gram of *alloc*innamic acid alone, 0.264 gram of  $\beta$ -truxillic acid was formed, whilst this quantity of *allo*acid when mixed with one gram of *n*-cinnamic acid had yielded 0.707 gram of  $\beta$ -truxillic acid.

This result is, therefore, quite in harmony with what was found previously.

This increased yield of  $\beta$ -truxillic acid on adding normal cinnamic acid to the *allo*acid was formerly explained by me by assuming that  $\beta$ -truxillic acid might be formed from one molecule of *allo*acid and one molecule of normal cinnamic acid. It is, however, obvious that we should observe the same thing when *n*-cinnamic acid itself was transformed into  $\beta$ -truxillic acid and when the *allo*acid formed  $\beta$ -truxillic acid indirectly over the *n*-cinnamic acid.

Up to the present, however, the transformation of *n*-cinnamic acid into  $\beta$ -truxillic acid has not been observed. RUBER <sup>1)</sup>, CIAMICIAN and SILBER <sup>2)</sup> and also myself when following RUBER's plan of illumination, could not demonstrate a formation of  $\beta$ -truxillic acid from *n*-cinnamic acid.

In order, however, to be able to make a choice of these two explanations, the following experiment was made.

On three dishes (diameter 18 cm.) of equal size and shape were distributed in the manner directed 1 gram of *allo*acid, 1 gram of *n*-cinnamic acid and  $\frac{1}{2}$  gram of *allo*acid +  $\frac{1}{2}$  gram of *n*-cinnamic acid, respectively. The illumination took place for two hours in sunlight; after each half hour, however, the acids were redissolved and recrystallised. The following quantities of  $\alpha$ - and  $\beta$ -truxillic acid were found to have formed.

	$\alpha$	$\beta$
1 gr. of <i>alloc</i> innamic acid	trace	0.073
1 gr. ,, cinnamic acid	0.117 <sup>3)</sup>	0.498
$\frac{1}{2}$ gr. ,, <i>allo</i> - + 1 gr. normal cinnamic acid	0.013	0.193

<sup>1)</sup> Ber. **35**, 2908 (1902).

<sup>2)</sup> Ber. **35**, 4128 (1902), **46**, 1564 (1913).

<sup>3)</sup> The transformation of *n*-cinnamic acid into  $\alpha$ -truxillic acid was first noticed by J. BERTRAM and KÜRSTEN [Journ. f. prakt. Chemie **51**, 324 (1896) and Ber. **28** IV, 387 (1896)].

A second experiment similarly conducted gave a concordant result. Hence, it appears that

a. normal cinnamic acid can yield  $\alpha$ - as well as  $\beta$ -truxillic acid,  
 b. the formation of  $\beta$ -truxillic acid takes place not primarily but secondarily over the normal acid,

c.  $\beta$ -truxillic acid is not formed by the union of 1 molecule of normal and one molecule of *allocinnamic* acid as was supposed formerly.

It was still required to ascertain the reason why the *modus operandi* applied by RIBER did not give  $\beta$ -truxillic acid.

According to this method the powdered cinnamic acid is spread out in a thin layer on a sheet of paper and placed in a photographic frame.

From the results of the following experiment it will be seen that the finely divided state of the cinnamic acid obstructs the formation of  $\beta$ -truxillic acid.

On sheets of paper were plotted surfaces of equal size. These sheets were placed on enfleurage frames and on each marked space were spread out 1 gram of cinnamic acid powdered or crystallised. After about an hour's exposure to light, both the powders and the crystals were treated as stated in the following survey. In all, the exposure occupied 5 hours.

	With		Without	
	glass covering	glass covering	glass covering	glass covering
	$\alpha$	$\beta$	$\alpha$	$\beta$
Powdered	0.364	nihil	0.650	nihil
„ mixing	0.260	„	0.705	„
Crystallised in porcelain dish and removed by scraping	0.120	0.044	0.321	0.150
Same, after being recrystallised in the same manner each hour	0.061	0.088	0.221	0.176

The glass used as covering and derived from photographic plates was not of uniform quality, hence the results obtained with glass covering are not mutually comparable.

The powdered cinnamic acid, both with and without glass covering, has always yielded  $\alpha$ -truxillic acid only. From the crystals  $\alpha$ - and  $\beta$ -truxillic acid have formed in both cases.

I hope, shortly, to revert to this remarkable transformation.

**Botany.** — “*On the mutual influence of phototropic and geotropic reactions in plants.*” By Dr. C. E. B. BREMEKAMP. (Communicated by Prof. F. A. F. C. WENT).

(Communicated in the meeting of March 27, 1915).

§ 1. *Introduction.*

It is conceivable that part of the quantity of unilaterally incident light which is just sufficient to cause a naked eye curvature in etiolated *Avena* coleoptiles, might be replaceable by a geotropic induction of shorter duration than the presentation time. Starting from this supposition Mrs. C. J. RUTTEN—PEKELHARING<sup>1)</sup> has carried out a number of experiments in which the seedling received both a light- and a gravitational stimulus, either simultaneously or in rapid succession and both lasting about two-thirds of what had been found to be the phototropic and the geotropic presentation time. These experiments gave uniformly negative results. Macroscopic curvatures were never observed.

Experiments of Mad. POLOWZOW<sup>2)</sup> and of MAILLEFER<sup>3)</sup> on geotropic curvatures and of ARISZ<sup>4)</sup> on phototropic ones, have shown that after a stimulus which had no macroscopic effect, deviations from the original position could nevertheless be demonstrated with suitable apparatus. In this connection the results of Mrs. RUTTEN's experiments are somewhat puzzling. An obvious deduction from them would be that light exercises an unfavourable influence on the gravitational reaction or, alternatively, gravity on the phototropic curvature. Before abiding by this conclusion, however, it is necessary to take another possibility into consideration.

Statements in the literature show, that in many cases a marked difference may be observed between the rates at which the phototropic and the geotropic reaction processes proceed. The gravitational curvature is generally visible sooner and reaches its maximum more quickly. When therefore the two stimuli are applied simultaneously or immediately after one another, there is every chance that the phototropic curvature will only have reached a very small value when the geotropic one has already passed its maximum and that, when

1) C. J. RUTTEN—PEKELHARING. Untersuchungen über die Perzeption des Schwerkraftreizes. *Recueil des Trav. Botan. Néerl.* Vol. VII. 1910.

2) W. POLOWZOW. Untersuchungen über Reizerscheinungen bei den Pflanzen. Jena 1909.

3) A. MAILLEFER. Etude sur la réaction géotropique. *Bull. Soc. Vaud. Sc. Nat.* XLVI. 1910. Nouvelle étude expérimentale sur le géotropisme. *ibidem* XLVIII. 1912.

4) W. H. ARISZ. *Proceedings K. Akad. v. Wet.* Amsterdam. 1911.

thereupon the light curvature begins to approach its maximum, there remain only traces of the other. There can in this case be no question of a clear reinforcement of the first reaction by the second. On the other hand, this reinforcement may be expected to be very pronounced, when so much time elapses between the stimuli that both curvatures reach their maxima at the same time.

It is convincingly proved by experiments which are described in the following section, that a complete summation does indeed take place in this last case. Moreover the surmise was confirmed that, when a small light-stimulus and a geotropic induction are applied simultaneously or in rapid succession, the geotropic curvature reaches its maximum before the phototropic one is clearly visible and has more or less disappeared again, when the latter has attained its greatest value. Mrs. RUTTEN's results thus find a simple explanation.

We must, however, guard against concluding from these data that there is no modification of the phototropic reaction, due to gravity, or of the geotropic curvature under the influence of light.

PFEFFER<sup>1)</sup> has already pointed out the possibility of such changes. Excepting, however, certain special cases relating to plagiotropic organs (e. g. rhizomes of *Adoxa*, in which case STAHL first showed a change in the geotropic reaction under the influence of light) this phenomenon has not been completely demonstrated. (Compare GUTTENBERG<sup>2)</sup>). I have succeeded in finding several examples of this in *Avena* seedlings. The reversal of the geotropic reaction after omnilateral illumination of certain duration may be put forward as a striking case. Details and discussion relating to these phenomena are embodied in sections 3 and 4.

## § 2. *Summation of phototropic and geotropic curvatures.*

After it had been found, in a number of preliminary experiments of which details may here be omitted, in what time light- and gravitational curvatures, as reactions to stimuli of definite strength, reached their maxima, I arranged the experiments in the following way.

I used for illumination a 10 candle-power Osram-lamp fed by an storage battery, which I kept constant at 10 volts. Since this had however drawbacks, the battery was strengthened later and the current was kept at the desired strength by the use of an adjustable

1) W. PFEFFER. *Planzenphysiologie*. 1 Aufl. 1881, Bd. 2, p. 338.

2) H. RITTER VON GUTTENBERG. Ueber das Zusammenwirken von Geotropismus und Heliotropismus in parallelotropen Pflanzenteilen. Pringsheim's Jhrb. XLV. 1908.

resistance. At a certain distance from the lamp were placed boxes of *Avena* seedlings which were always put in such a position that their longitudinal axis made a small angle with the direction of the rays of light, so that the seedlings which to the number of 17 to 20 stood in each box in one row, did not shade each other. For the geotropic stimulation the boxes were put upright on one of the narrow sides. For further details reference must be made to the fuller communication, which will appear later.

The apparatus was placed in a part of the laboratory greenhouse at Utrecht fitted up as dark room, where arrangements for ventilation and warming make it possible to carry out experiments at constant temperature and in pure air. In this case the temperature was kept at 21° C.

A series of experiments was generally carried out with six boxes. Nos. 1, 2, 3, and 4 were stimulated phototropically for six or ten seconds; No. 1 at a distance of 70 cm. from the lamp, the other ones at one metre. The geotropic stimulation of boxes 3, 4, and 5 began 50 minutes after the illumination and lasted 20 minutes (in some series 15 min.). Box 3 was placed upright in such a way that the side which during illumination had been in front, was now underneath, whilst with box 4 the front of the illumination came uppermost; 6 had already been placed upright 20 (in other cases 15) minutes earlier and remained 40 (or 30) in this position. Two hours after illumination, i.e., 50 minutes after the end of the geotropic stimulation, the light as well as the gravitational curvature had reached its maximum; at that moment their magnitude was noted. For this I used a method recommended by LINDNER<sup>1)</sup>, in which a lamp, placed at a sufficient distance, throws a shadow of the box on a strip of bromide paper, stretched immediately behind. This was later developed and preserved as protocol of the experiment. The horizontal deviation from the apex in mm. served as a measure of the curvature.

In order to ascertain how far the average deviation of the 17—20 seedlings in one box furnished a sufficiently reliable value, five boxes were stimulated in the same way phototropically and geotropically: first illuminated unilaterally for six seconds with an intensity of 10 M. C. and then 50 minutes afterwards placed upright and left for 20 minutes in this position. After 2<sup>1</sup>/<sub>4</sub> hours the deviations in m.m. amounted to:

3.2, 3.2, 3.2, 3.3 and 3.3.

<sup>1)</sup> P. LINDNER, Ber. d.d. Bot. Ges. XXXII, 4, 1914.

The values found in the experiments are collected in the following table. Each horizontal line represents a separate series. The figures in brackets indicate the magnitude of the light stimulus in metre candle seconds (MCS) and the duration of the gravitational stimulus in minutes.

	1	2	3	4	5	6
I	2.8 (200)	2.6 (100)	—	3.6 (100+15 min.)	0.8 (15 min.)	1.3 (30 min.)
II	2.5 (120)	1.9 (60)	1.0 (60—15 min.)	2.2 (60+15 „)	0.4 (15 „)	1.6 (30 „)
III	2.3 (120)	2.1 (60)	—	3.2 (60+15 „)	1.0 (15 „)	1.6 (30 „)
IV	2.7 (120)	2.5 (60)	0.5 (60—20 „)	3.1 (60+20 „)	1.7 (20 „)	2.9 (40 „)
V	2.2 (120)	1.6 (60)	—0.2 (60—20 „)	2.5 (60+20 „)	1.4 (20 „)	2.1 (40 „)
VI	2.4 (120)	2.1 (60)	1.2 (60—20 „)	3.4 (60+20 „)	1.2 (20 „)	2.6 (40 „)
VII	2.0 (120)	1.4 (60)	—0.2 (60—20 „)	2.6 (60+20 „)	1.2 (20 „)	2.0 (40 „)

The fairly considerable divergence which sometimes occurs between the series, is explained by the difference in length of the seedlings used; thus those of IV were very tall, those of VII very short; in connection with this comparison should be made with ARISZ' data<sup>1)</sup> for phototropic curvatures and with MAILLEFER'S detailed tables for geotropic ones (1912 l.c.).

When the experiments were taking place it could be noted that the phototropic curvatures were often already visible before the end of the gravitational stimulation. In those seedlings in which light- and gravitational curvatures acted in opposite direction, the phototropic one extended already lower down, at the moment when the geotropic one became visible at the apex, so that the coleoptile temporarily acquired a weak S-shaped bend.

As the figures show, the curvature which arises when light and gravity bring about deviations in the same direction, more or less equals the sum of the curvatures which each stimulus calls forth, when acting separately. When they act in opposition to one another, then the resulting deviation is approximately the same as the difference of the separate deviations. In the following table the relative figures are once more placed side by side with the sums and differences calculated from 2 and 5 placed between brackets after those found.

<sup>1)</sup> W. H. ARISZ. Onderzoekingen over fototropie. Diss. Utrecht, 1914.

	2	5	4	3
I	2.6	0.8	3.6 (3.4)	—
II	1.9	0.4	2.2 (2.3)	1.0 (1.5)
III	2.1	1.0	3.2 (3.1)	—
IV	2.5	1.7	3.1 (4.2)	0.5 (0.8)
V	1.6	1.4	2.5 (3.0)	-0.2 (0.2)
VI	2.1	1.2	3.4 (3.3)	1.2 (0.9)
VII	1.4	1.2	2.6 (2.6)	-0.2 (0.2)

This complete summation is all the more remarkable when the figures are compared with those of the illumination with the double amount of energy. These remain everywhere behind the summation curvatures. We find here a confirmation of the surmise that the phototropic curvature does not remain below a certain maximum in consequence of increased mechanical resistance, but that in reality under the influence of the illumination there occurs a change of condition in the plant, whereby the phototropic curvature with increase of the stimulus finally again diminishes and may even attain negative values, as CLARK<sup>1)</sup> and ARISZ<sup>2)</sup> have shown for *Avena*.

If the gravitational stimulus is applied immediately after illumination, then the geotropic curvature has almost completely disappeared when the phototropic one reaches its maximum. A single example will suffice to show this.

Deviations in mm.  $2\frac{1}{4}$  hours after the beginning of the experiment:

2	3	4	5
1.6 (40)	1.3(40 - 20 min.)	1.9(40+20 min.)	0.4 (20 min.)

The maximal geotropic curvature 50 minutes after the cessation of stimulation amounted in this case to about 1.5 mm. The small deviation which still remains after  $2\frac{1}{4}$  hours, shows itself clearly however in the figures of 3 and 4.

In some experimental series the boxes were placed on the clinostat before and after stimulation in order to eliminate the opposing

<sup>1)</sup> O. L. CLARK. Über negativen Phototropismus bei *Avena sativa*. Zeitschr. f. Bot. V. 1913.

<sup>2)</sup> W. H. ARISZ. Proceedings K. Akad. v. Wet. Amsterdam. October 1913.

effect of gravity.<sup>1)</sup> It is of little importance in this case whether the stimuli are applied immediately after one another or with a certain interval between them. The speedy falling off of the curvature, as soon as it has reached its maximum, is not observable in plants which turn on a horizontal axis. On the other hand the phototropic reaction goes on for so much longer than the geotropic one (a difference of hours) that it is experimentally impossible to make the maxima coincide. We must in this case therefore limit ourselves to establishing that the curvature of seedlings to which both stimuli have been applied, according as they have acted to reinforce or counteract each other, equals the sum or the difference of the curvatures which are shown by two groups of controls of which one is only illuminated and the other only stimulated geotropically. This is found to be possible at any moment, chosen arbitrarily. In the following example the geotropic stimulation was administered 50 minutes after the phototropic and the record was made 5 hours after the commencement of the experiment.

2	3	4	5
7.7 (100)	5.5(100 - 20 min.)	11.1(100 + 20 min.)	3.3 (20 min.)

Since it might be considered objectionable when dealing with such marked curvatures to take the horizontal deviation of the apex as a measure, I have in addition determined the angle of the curvature. For the sake of simplicity I considered the curvature as a circular arc, to which the lines bisecting the base and the apex — which latter at this moment has become straight again, — are tangents. The supplement of this arc gives an idea of the distance travelled. This amounts to:

2	3	4	5
47°	35°	66°	15°

There is here therefore also a complete summation.

The experiments which are described in this section, lead to the following conclusion:

<sup>1)</sup> In very small curvatures, it is principally the longitudinal component which opposes the reaction. Cf. § 4.

The reactions to small light and gravitational stimuli do not noticeably influence each other.

§ 3. *Changes in the phototropic and geotropic reactions under the influence of light.*

Up to this point we only used unilateral illumination of fairly slight intensity. The question now is whether other results are obtained by the application of greater quantities of light. By changing the duration of illumination as well as its intensity it is possible to bring about modifications in the phototropic reaction which for our purpose we may arrange in two different categories: 1. reversal of the direction of the curvature and 2. change in the rate of reaction. If we wish to know how a definite phototropic curve at its maximum extent is combined with a maximal geotropic deviation, we have only to determine the length of time after which the maximal light-curve is reached and then to administer the two stimuli with such an interval that the curvature maxima coincide.

In carrying out these experiments it is found to be quite immaterial whether we are concerned with a positive phototropic curvature or one in the opposite direction and whether the maximum is reached after a shorter or longer time. Summation always takes place.

This is, however, not the end of the process. If, after stimulation, the seedlings are placed on the clinostat and observation is continued for a considerable time, then one begins to note deviations, at least when there has not been too great an interval of time between the two stimulations. By summation of curvatures of the same direction apex curvatures finally occur in opposite direction and seedlings in which opposite curvatures have been induced, sometimes show stronger curvatures.

The same phenomenon was to be observed when unilateral was replaced by omnilateral illumination.

During illumination which in different experiments was varied in strength as well as in duration, the seedlings were rotated at constant velocity round their axis. When illumination ceased, they were immediately placed in a horizontal position and stimulated geotropically for some time.

Already in the first series of experiments differences were obvious. The distance from the Osram lamp of 10 candle power amounted in this case to 2 metres. The times of illumination are in the following table placed in the top line, with the product of intensity and duration in metre-candle-seconds (M.C.S.) placed between brackets. The last box was not illuminated beforehand. The geotropic induction lasted

20 minutes. Examination took place 55 minutes after its end. As in the former section the horizontal deviation of the apex in mm. is given as a measure of the curvature.

20 min. (3000)	10 min. (1500)	5 min. (750)	2.5 min. (375)	1 min. (150)	30 sec. (75)	—
0.5	0.7	0.8	0.7	0.9	1.4	1.4

These figures were confirmed in different series of experiments. In these it was further noticed that the curvatures arose everywhere at the same time and at first also increased at the same rate.

Thus further observations were suggested with the object of seeing to what these differences arising in the course of the curvature-process might lead.

In the following table the magnitude of curvature after 40 minutes and after 2 hours are placed side by side.

Duration of illumination	Strength of illumination	Product M.C.S.	Curvature	
			After 40 min.	After 2 hours
300 sec.	2.5 MC	750	0.8	-0.9 (0.1)
150 "	2.5 MC	375	1.5	-0.4 (1.1)
180 "	1/8 MC	22.5	2.0	—
90 "	1/8 MC	11.25	2.1	—
Not illuminated			2.0	-0.0 (1.4)

The duration of the geotropic stimulation amounted to 30 min. Seedlings which were illuminated beforehand with 750 and 375 M.C.S., showed a clear S-shape after 2 hours. The apex of those that were not illuminated, was quite straight. The figures given are the apex-curvatures. Placed after in brackets are the figures which indicate the amount of the remainder of the original curvature, calculated on the assumption that the apex was straight. The antagonistic geotropic curvature was not yet measurable as is shown by the last line. The curvatures of the previously illuminated seedlings cannot therefore be ascribed to this cause. Experiments in which, after the cessation of geotropic stimulations, plants were placed on the clinostat, have indeed convincingly proved that without

the unilateral opposition of gravity, curvatures arise in a contrary direction in plants previously illuminated omnilaterally.

These experiments can be simplified by illuminating the seedlings from above instead of making them perform a certain number of revolutions during illumination. This has been done in all subsequent experiments. The quantity of light is again given in M.C.S.; in connection with this it should be remembered that it of course makes a difference to the plant whether the uppermost part of the apex only is constantly exposed to the light or whether successively the whole surface. Further, another sort of incandescent lamp was used in these experiments.

Geotropic stimulation lasted 30 minutes. After this removal to the clinostat. Examination 3½ hours after the completion of stimulation.

Duration of illumination	Strength of illumination	Product MCS	Curvature
16 min.	8 MC	4000	- 1.0
4 "	8 MC	1000	- 1.1
1 "	8 MC	250	+ 0.7
15 sec.	8 MC	60	+ 1.6
—	—	—	+ 1.6

In other experiments the duration of the geotropic stimulation was changed, e. g.:

Time of illumination 20 min., strength 8 M.C., product 5000 M.C.S.  
Horizontal during

40 min.	20 min.	10 min.	5 min.
- 0.9	- 2.5	- 2.0	- 1.8

(3 hours on the clinostat).

As is seen, the result is only slightly dependent on the duration of the geotropic stimulation.

The fact that in 40 min. a great deviation is observed, is undoubtedly connected with the fairly rapid cessation of the influence of preliminary illumination. When half-an-hour is allowed to elapse between illumination and geotropic stimulation, the influence of the first factor can no longer be demonstrated with certainty. This result is in remarkable agreement with the rapid disappearance of the

phototropic change of sensitiveness after preliminary illumination (ARISZ 1914 l. c. "fading of the excitation").

CLARK l. c. has described experiments in which a unilateral geotropic stimulation was followed by omnilateral illumination. Under these conditions also there occurs a curvature in contrary direction. With regard to the nature of the curvature which arises, it is difficult to form a definite judgment by this method of experimentation, because the geotropic stimulation induces a dorsiventrality (as yet not outwardly visible). A dorsiventral organ can, however, quite easily react to an omnilaterally symmetrical stimulus with a curvature of definite direction. In connection with the experiments described above it is however indeed probable that the curvatures mentioned by CLARK correspond to those observed in the present investigation.

May we now regard these curvatures as positively geotropic? Before answering this question, we may briefly examine the curvatures of opposite direction which arise in other cases and consider whether it is possible to form a simple conception of the way in which they arise. I have chosen *Avena* coleoptiles for a further analysis, because in their case inverse phototropic curvatures are very easily obtainable.

In ARISZ' experiments (l. c. 1914), in which the seedlings were given an omnilateral preliminary illumination of varying duration, it was found that the sensitiveness rapidly diminished at the beginning, and after more prolonged illumination increased again somewhat.

If the intensity of illumination was also varied, then the initial decrease in sensitiveness was seen to take place more rapidly according as the seedlings were exposed to stronger light, whilst the return of sensitiveness was thereby slightly delayed. Since when illumination is unilateral the front absorbs part of the light, the back receives less light. The consequence of this is that there the sensitiveness during illumination declines less markedly than in the front. When therefore after some time the sensitiveness of the front has more or less disappeared, the reaction of the posterior side can predominate. The result must then be a curvature away from the source of light.

In order to find out whether the here postulated differences in sensitiveness of the anterior and posterior sides can actually be observed, I have made a series of experiments in which three groups of boxes were always compared. The first group consisted of one box, the other two of from four to eight. The experiment began with an equally long and equally strong unilateral illumination of all the boxes. Afterwards the box of the first group was placed in

the dark and those of the other two groups stimulated again with different quantities of light, one group from the same side as before, the other from the opposite side. Finally, the curvatures obtained were compared. In this way I succeeded in showing that after a unilateral illumination sometimes important differences in sensitiveness of the posterior and the anterior sides occur. These are greatest in the neighbourhood in which the negative curvature begins to arise. Further data on this point will be published later.

We arrive therefore at the conclusion that the curvature away from the source of light arises, because the sensitiveness of the anterior side diminishes more quickly than that of the posterior and consequently the reaction predominates at the back.

This leads us further to deny the possibility of any direct comparison of this curvature with the negative phototropic reaction of roots which is not preceded by a positive one<sup>1)</sup> and remains on continued illumination. We ought therefore henceforth to distinguish the curvatures of contrary direction which occur in *Avena* coleoptiles by another name. They may be called *antiphototropic*.

Is it now possible to explain in the same way the contrary curvatures which arise when coleoptiles of *Avena* are stimulated geotropically after preliminary omnilateral illumination and the negative geotropic curvatures which JOST and Miss STOPPEL<sup>2)</sup> were able to observe in roots of *Lupinus albus* which were exposed to high centrifugal forces? Evidently not. The difference of pressure must always be the same in the cells of the upper and lower side. A

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1) K. LINSBAUER and V. VOUK. (Zur Kenntnis des Heliotropismus der Wurzeln. Vorl. Mitteilung. Ber. d. d. bot. Ges. Bd. 27. 1909) have stated that in roots of *Sinapis alba* and *Raphanus sativa* small intensities of light cause positive curvatures and greater intensities negative ones. Vouk has described these experiments somewhat more fully (Zur Kenntnis des Phototropismus der Wurzeln. Sitzungsber. d. K. K. Akad. d. Wiss. zu Wien Bd. 121. Abt. I. 1912). It results from this that the positive phototropic curvatures which these investigators observed in *Sinapis alba*, arose when there was illumination for 15 hours with an intensity of 0.64 M.C.; therefore by a quantity of light of 34,560 M.C.S. Vouk on page 503 gives a table, in which are found different examples of illumination with 128 M.C. during 5 minutes, by which means a quantity of light amounting to 38,400 M.C.S. was applied. The occurrence of a positive curvature is nowhere mentioned. Moreover with illumination lasting 2 minutes no positive curvature arose either. This discrepancy permits us to doubt the phototropic nature of the curvatures found. It is moreover quite unintelligible why even in the most favourable case not more than 71% of the roots reacted in this manner.

2) L. JOST und R. STOPPEL. Studien über Geotropismus II, Zeitschr. für Bot. Bd. IV. 1912.

direct reversal of the reaction would only be possible through a reversal of the polarity of the cells, a hypothesis far from simple and hitherto not susceptible of experimental verification. For this reason I may direct attention to another possibility.

In the cells which are given preliminary illumination, phototropic reactions are in progress which cannot lead to curvatures, because they keep each other in equilibrium. In consequence of the geotropic stimulation this equilibrium is now upset. It might be imagined, for example, that the geotropic stimulation displaces or destroys a substance necessary for the phototropic reaction. The resulting curvature would in reality therefore be phototropic. It is not impossible that also in the experiments of JOST and Miss STOPPEL an omnilateral stimulation (perhaps hydrotropic) thus expresses itself as a curvature.

§ 4. *Changes of the geotropic and phototropic reactions  
under the influence of gravity.*

According to MARIE-MARTHE RISZ<sup>1)</sup> an omnilateral gravitational stimulus has no effect on the sensitiveness with respect to a subsequent unilateral one. From the data in the second part of her paper, however, one may deduce that this is not correct. For Miss RISZ there proves, that the component of gravity in the direction of the organ<sup>2)</sup> weakens the reaction. After an omnilateral gravitational stimulus acting at an angle of 90° and having therefore a longitudinal component equal to 0, the reaction must be stronger than when the plant is placed vertically for the stimulation (longitudinal component + mg.). This was indeed the case in my own experiments.

Some boxes rotated for a certain time round the horizontal axis of the clinostat and were subsequently subjected to a unilateral gravitational stimulus simultaneously with a control box. I examined the curvatures forty minutes after the end of stimulation.

Differences such as those found here, are also observable when the boxes are placed for some time in the reverse position (longitudinal component — mg.).

Duration of unilateral geotropic stimulus 30 minutes.

Previously placed on the clinostat during.

<sup>1)</sup> MARIE-MARTHE RISZ. Über den Einfluss allseitig und in der Längsrichtung wirkender Schwerkraft auf Wurzeln. *Jhrb. f. wiss. Bot.* LIII. 1913.

<sup>2)</sup> I already pointed out in 1912 the importance of this component. Die rotierende Nutation und der Geotropismus der Windepflanzen. *Rec. d. Trav. Bot. Néerl.* IX. p. 298—301.

2 hours	1 hour	1/2 hour	Control
—	2.5	2.2	2.1
1.7	1.7	1.8	1.5
2.7	—	—	2.3

Much more distinct differences occur when transverse and longitudinal gravitational stimuli are applied simultaneously. A slight modification of Miss Risz' procedure enables us to demonstrate also the influence of the longitudinal component, when the latter has a negative value. With this object two boxes are placed parallel to the vertical axis of the centrifuge so that the seedlings in one box have their apices turned towards the axis, in the other away from it. If now such a revolution-velocity is given to the axis as to apply to the seedlings a force  $mg$ , then the longitudinal component for the first box is  $+mg$ , and for the second  $-mg$ . Furthermore gravity acts on the seedlings at the same time. After centrifuging the boxes were again placed in their original position. A box which for the same length of time had been horizontal, served as control, since in this case the longitudinal component is 0.

With a stimulation of 30 minutes the curvatures were 40 minutes after its cessation:

$-mg$	C	$+mg$
2.9	1.6	0.2
3.4	1.5	0.3
3.9	2.2	0.9

If a unilateral light-stimulus is applied after an omnilateral gravitational stimulus, then similar differences can be observed.

For this the boxes are again placed on the centrifuge, whose axis this time is horizontal. After 30 minutes centrifuging the seedlings are illuminated during 6 seconds with an intensity of 10 M.C. The control box, which remained in its ordinary position, was naturally subjected to the same conditions as the seedlings on the centrifuge, which had their apices pointing towards the axis. In both cases the longitudinal component was  $+mg$ .

After 2 hours the curvatures amounted to :

- mg	C	+ mg
2.5	1.5	1.5

The influence of the longitudinal component is therefore once more evident.

The term longitudinal component of gravity is of course only a phrase. No way of explaining it physiologically has so far been found.

The phototropic curvatures of the coleoptiles of *Avena* when illuminated at different angles, showed a very marked deviation from the expected sine relation. As ARISZ (l. c. 1914) has justly argued, the paraboloid shape of the apex must be a very important factor in this connection.

In geotropic reactions another factor must also be taken into account, namely, the polarisation of separate cells.

It is generally assumed that a difference exists in the sensitiveness to pressure of the protoplasm lining the inner and the outer walls of the cells. The idea that there may be a similar difference of sensitiveness between the apical and basal part of each cell, may therefore not be summarily rejected. In this way the longitudinal component can also be explained. In the rotating apices of climbing plants where I could establish its influence on growth as well as on the nature of geotropic curvature, this is probably the right conception. The paraboloid vegetation point of a stem which bents at its end like a hook, may here take up any sort of position and hardly deserves consideration in connection with gravitational stimuli.

*Utrecht, March 1915.*

*Botanical Laboratory.*

**Astronomy.** — “*On the mean radius of the earth, the intensity of gravity, and the moon’s parallax.* By Prof. W. DE SITTER.

1. NEWCOMB has more than once<sup>1)</sup> pointed out that the mean radius of the earth is more appropriate for use as a standard of reference, than the equatorial radius, which is always used in astronomical practice. The mean radius in fact, which — if we neglect quantities of the second order in the compression — is also the mean radius of curvature, is more nearly the quantity actually

<sup>1)</sup> Researches on the motion of the moon, second paper, page 41  
Tables of the sun, page 12, footnote.

determined by geodetic measures, which are practically all made in mean latitudes.

The several definitions of the mean radius<sup>1)</sup> are identical to the first order of the compression  $\epsilon$ . I adopt as mean radius the radius at the geographical latitude whose sine is  $\sqrt{1/3}$ , and which is given by the formula

$$r_1 = b [1 - \frac{1}{3} \epsilon + \frac{5}{9} \epsilon^2 + \dots] \dots \dots (1)$$

HELMERT has recently<sup>2)</sup> collected the following determinations of  $b$ , from which I derive the value of  $r_1$  by means of the corresponding value of  $\epsilon$ .

1. From four European arcs, all reduced with BESSEL'S  $\epsilon^{-1} = 299.15$ .

$$b = 6378150 \qquad r_1 = 6371077$$

2. From arcs in India and South-Africa, reduced with  $\epsilon^{-1} = 298.3$ .

$$b = 6378332 \qquad r_1 = 6371237$$

3. From the geodetic measures in the United States, reduced with  $\epsilon^{-1} = 296.96$ .

$$b = 6378388 \qquad r_1 = 6371268$$

It will be seen that the agreement of the several values of  $r_1$  is much better than of  $b$ .

Combining these values of  $r_1$  with the weights assigned by HELMERT to the corresponding values of  $b$ , we find

$$r_1 = \mathbf{6371237} \pm \mathbf{49} \dots \dots (2)$$

The mean error has been derived from the residuals. If the values of  $b$  are combined in the same way we find from the residuals the mean error  $\pm 66$ .

2. A similar reasoning applies to the acceleration of gravity. HELMERT<sup>3)</sup> finds

$$g = 9.78030 \{1 + 0.005302 \sin^2 \varphi - 0.000007 \sin^2 2\varphi\}.$$

<sup>1)</sup> HELMERT, Höhere Geodäsie, I, pages 64—68.

<sup>2)</sup> Geoid und Erdellipsoid. Zeitschr. der Ges. für Erdkunde, 1913, page 17.

<sup>3)</sup> Encyclopädie der Math. Wiss.; Band VI. 1 B, Heft 2, page 95. The alternative formula given there, viz.:

$$g = 9.78028 \{1 + 0.005300 \sin^2 \varphi - 0.000002 \sin^2 2\varphi\}$$

must be dismissed, since for theoretical reasons the coefficient of  $\sin^2 2\varphi$  must be included between the limits  $-0.0000055$  and  $-0.0000088$ . The theoretical expression of the coefficient is  $+\frac{1}{4} \epsilon^2 - \frac{5}{2} \epsilon \rho - \frac{10}{3} \frac{5}{2} B_4$ , where  $B_4$  is necessarily positive, and smaller than  $\frac{1}{7} J$ . Taking  $\epsilon = 0.00338$ ,  $\rho = 0.00345$ ,  $J = 0.00165$ , we find the stated limits. The value of the coefficient in the formula of the text corresponds to DARWIN'S value of  $B_4$  viz; 0.0000029.

For  $\sin^2 \varphi_1 = 1/3$ , this gives

$$g_1 = 9.79752. \quad \dots \quad (3)$$

HAYFORD and BOWIE<sup>1)</sup> have

$$g = 9.78038 \{1 + 0.005304 \sin^2 \varphi - 0.000007 \sin^2 2\varphi\},$$

from which

$$g_1 = 9.79762.$$

The fundamental determination at Potsdam by KÜHNEN and FURTWÄNGLER, viz:  $g_P = 9.81274$ , combined with the value of  $\varepsilon$ , which will be derived in the following paper, viz:  $\varepsilon^{-1} = 296.0$ , gives

$$g_1 = 9.79755 \quad \dots \quad (3')$$

I adopt<sup>2)</sup> this last value (3').

We then find the attraction of the earth by the formula

$$g'_1 = \frac{fM}{r_1^2} = g_1 \left\{ 1 + \frac{2}{3} Q_1 + \frac{10}{3} \varepsilon^2 - \frac{122}{63} \varepsilon Q_1 - \frac{145}{36} B_4 \right\}, \quad (4)$$

where

$$Q_1 = \frac{\omega^2 r_1^3}{fM} = \frac{\omega^2 r_1}{g'_1} = 0.0034496^3),$$

$$\varepsilon = 0.00338, \quad B_4 = 0.0000029,$$

which gives

$$g'_1 = \mathbf{9.82014} \quad \dots \quad (5)$$

3. Now let  $\pi' = \frac{\sin \pi}{\sin 1''}$  be the constant of the lunar parallax.

By BROWN'S theory we have

$$\pi' = [0.0003940] \frac{b}{a},$$

where the number in square brackets is a logarithm, and by KEPLER'S third law

$$a^3 n^2 = fM (1 + \mu)^4).$$

We find thus

1) Effect of Topography and Isostatic compensation upon the intensity of gravity (second paper) U. S. Coast and Geod. Survey, special publ. No. 12, page 25.

2) In the original Dutch communication the value (3) was adopted. The difference is negligible.

3) The quantity which is commonly used is

$$Q_0 = \frac{\omega^2 b}{g_0} = Q_1 + \frac{3}{2} Q_1^2 = 0.0034676.$$

4) Strictly speaking this value of  $M$  is not exactly the same as that used in (4), since the latter is exclusive of the atmosphere. The mass of the atmosphere is 0.000000865  $M$ . The effect on  $\pi'$  is 0".001.

$$\pi'' = \frac{[0.0011820]}{\sin 1''} \cdot \frac{n^2}{1+\mu} \cdot \frac{b^3}{r_1^3} \cdot \frac{r_1}{g_1'} \dots \dots \dots (6)$$

Using now the value (1) of  $b$ , or

$$\frac{b}{r_1} = (1 + \frac{1}{3} \epsilon) (1 - \frac{4}{3} \epsilon^2),$$

and the values (2) and (5) of  $r_1$  and  $g_1'$ , and taking

$$\mu^{-1} = 81.50 \pm 0.07$$

we find

$$\pi' = 3418''.695 (1 + \frac{1}{3} \epsilon) \dots \dots \dots (7)$$

The uncertainty of the numerical factor may be estimated as follows :

- due to  $r_1$  . . . .  $\pm 0''.008$
- „ „  $g_1$  . . . .  $\pm 0''.006$
- „ „  $\mu$  . . . .  $\pm 0''.010$ .

In the following paper we will derive the value

$$\epsilon^{-1} = 296.0 \pm 0.2.$$

This gives

$$\pi' = 3422''.544 \pm 0''.015 \dots \dots \dots (8)$$

The mean error includes the effects of  $r_1$ ,  $g_1$  and  $\mu$  as given above, to which has been added :

$$\text{due to } \epsilon \dots \dots \pm 0''.0025.$$

From the recent determination of the lunar parallax by the observatories at Greenwich and the Cape <sup>1)</sup> — assuming the corrections given to be applicable to HANSEN'S parallax 3422''.07 — we find the following comparison :

$\epsilon^{-1}$	<i>Cape-Greenwich</i>	<i>Formula (7)</i>
293	3422''.60	3422''.58
294	.54	.57
295	.48	.55
296	.42	.54 <sup>s</sup>
297	.36	.53.

This would give :

$$\epsilon^{-1} = 293.4, \quad \pi' = 3422''.58.$$

With  $\epsilon^{-1} = 296.0$  would correspond the observed value  $\pi' = 3422''.42$ , which is 0''.12 smaller than (8). It does not appear impossible to ascribe this quantity to errors of observation, especially to a constant error of pointing on the Crater Mösting A by the observers at Greenwich and the Cape.

<sup>1)</sup> Monthly Notices, Vol. LXXI, page 526.

The equation (6) has in the course of time been used for the determination of  $\mu$ , of  $r_1$  and of  $\epsilon$ . It is, however, doubtful whether the accuracy, needed to derive a real correction to our present knowledge of any of these constants, could be attained even by a series of observations such as is proposed by E. W. BROWN in his address to the British Association in Australia. It certainly should determine the parallax within a fraction of  $\pm 0''.01$  to be of real value. To make this possible the selenocentric coordinates, especially the radius-vector of the Crater Mösting A, or any other feature of the lunar surface which is used for the determination, must be accurately known. The determinations of the height of Mösting A over the mean radius are:

$$\text{HAYN } ^1) \quad + 2''.2 \pm 0''.6 \quad \text{effect on } \alpha' \dots 0''.037$$

$$\text{STRATTON } ^2) + 3''.0 \pm 0''.7 \quad ,, \quad ,, \quad ,, \quad \dots 0''.049.$$

The difference between the two determinations makes a difference in the parallax larger than the uncertainty due to any of the constants  $r_1$ ,  $g_1$ ,  $\mu$  or  $\epsilon$ .

Our conclusion is thus that the value (8) of the lunar parallax is more accurate than any that can at present be derived by direct observations.

**Geodesy.** — “*On Isostasy, the Moments of Inertia, and the Compression of the Earth*”. By Prof. W. DE SITTER.

1. The hypothesis of isostasy is strictly speaking a compound of two hypotheses, viz.:

A. Up to a certain distance from the centre the constitution of the earth is in agreement with the theory of CLAIRAUT; i. e. the equipotential surfaces are surfaces of equal density, and the density never increases<sup>3)</sup> from the centre outwards. [Apart from this condition it may vary in any manner, even discontinuously.] The last

<sup>1)</sup> Selenographische Koordinaten. III. (1907). Abh. der K. Sächs. Ges. der Wiss. Band XXX. page 74.

<sup>2)</sup> Memoirs of the R. A. S. Vol. LIX, Part IV, page 276.

<sup>3)</sup> Strictly speaking it is not necessary that always  $\frac{d\Delta}{db} \leq 0$ . It is sufficient if, for

$$\text{all values of } b, \int_0^b \beta^2 \frac{d\Delta}{d\beta} d\beta \leq 0, \text{ and } \int_0^b \beta^3 \epsilon \frac{d\Delta}{d\beta} d\beta \leq 0.$$

equipotential surface which satisfies these postulates is called the *isostatic surface*, and will be denoted by  $S_0$ .

B. In the crust outside  $S_0$  the distribution of mass is such that over sufficiently large areas of  $S_0$  there is the same mass as there would be with a certain normal distribution. How exactly this normal distribution is supposed to be, is generally not explicitly stated. In any case with the normal distribution the whole mass of the crust would be inclosed between  $S_0$  and a certain *normal surface*  $S$ .

The actual surface of the earth is neither an equipotential surface, nor a surface of equal density. The actual surfaces of the oceans may be supposed to be parts of one and the same equipotential surface, which is called the *geoid*. The figure of this geoid is derived from geodetic measures made on the continents or from determinations of the intensity of gravity made on the continents and on the sea. It has been found that the geoid differs very little from an ellipsoid of revolution. This "ellipsoid of reference" may be taken to be identical with the normal surface, or more precisely the several ellipsoids of reference found from each separate investigation are considered to be approximations to the normal surface. The latter is thus determined as the ellipsoid best fitting the several partial ellipsoids of reference.

2. On the basis of the theory of isostasy we must consider the isostatic surface  $S_0$  as primarily given, though of course its figure is unknown, and must be determined from that of  $S$ . Now the relation between  $S_0$  and  $S$  is not very explicitly stated by the different authors on the subject.

The most natural assumption evidently is that  $S$  would be a equipotential surface and a surface of equal density. The normal surface satisfying these conditions, which are those of the theory of CLAIBAUT, will be called the *ideal surface* of the earth, and will be denoted by  $S_1$ .

When HELMERT originally introduced the method of condensation, he supposed the radius-vector of the surface of condensation to be proportional to that of the normal surface:  $r_0 = r(1-a)$ . In the reductions according to the theory of isostasy the isostatic surface  $S_0$  corresponds to HELMERT'S surface of condensation. The normal surface would then be given by  $r = r_0(1-a)^{-1}$ . This surface may be called the *proportional surface*, and will be denoted by  $S_2$ .

Some authors also state as a definition that the depth of the isostatic surface below the normal surface is constant. We should thus have  $r = r_0 + Z$ . The surface so defined may be called the *equidistant surface*, and will be denoted by  $S_3$ .

Let

$b$  = the equatorial radius } of any surface,  
 $\varepsilon$  = the compression

Further

$$\eta = \frac{b}{\varepsilon} \frac{d\varepsilon}{db},$$

then we have approximately

$$\varepsilon_1 - \varepsilon_0 = \frac{\eta \varepsilon}{b} (b_1 - b_0).$$

For the earth we have  $\eta_1 = 0.561$ . Taking  $\frac{b_1 - b_0}{b} = 0.0179$ , and  $\varepsilon = 0.00338$ , we find

$$\varepsilon_1 - \varepsilon_0 = + 0.000034$$

The difference of the numerators is

$$\varepsilon_1^{-1} - \varepsilon_0^{-1} = - 3.0^1).$$

<sup>1)</sup> A better approximation is obtained by also taking into account the variation of  $\nu$ . Let

$\Delta$  = the density at } any equipotential surface,  
 $D$  = the mean density within

and

$$\zeta = - \frac{b}{D} \frac{dD}{db},$$

then the theory of CLAIRAUT gives, neglecting the second order in  $\varepsilon$

$$\zeta = 3 \left( 1 - \frac{\Delta}{D} \right)$$

$$b \frac{d\eta}{db} = 2\zeta(1 + \eta) - 5\eta - \eta^2.$$

If the crust were constituted in accordance with the theory of CLAIRAUT, it would consist of a solid crust entirely covered by an ocean of a depth of about 2.4 km. The bottom of this ocean would be an equipotential surface, say  $S_b$ . For  $S_1$  we have now

$$\Delta_1 = 1.03 \quad D_1 = 5.52$$

from which we find

$$\zeta_1 = 2.44.$$

Then, with  $\eta_1 = 0.561$ , we find

$$b_1 \left( \frac{d\eta}{db} \right)_1 = 4.50.$$

Therefore, since  $b_1 - b_0 = 0.00038 b_1$ , we have

$$\eta_b = \eta_1 - (b_1 - b_0) \left( \frac{d\eta}{db} \right)_1 = 0.559.$$

For the surface  $S_b$  we then have

For the proportional surface we have, of course,

$$\varepsilon_2 = \varepsilon_0.$$

The equidistant surface is not an exact ellipsoid, but it differs only in quantities of the second order in  $\varepsilon$  from the ellipsoid whose compression is,

$$\varepsilon_3 = \frac{\varepsilon_0}{1 + \frac{1}{3}\varepsilon_0 + k} = 0.979 \varepsilon_0.$$

where  $k = \frac{Z}{b}$ . Therefore

$$\varepsilon_3 - \varepsilon_0 = -0.000070$$

$$\varepsilon_3^{-1} - \varepsilon_0^{-1} = +6.1.$$

The depth of the isostatic surface below the normal surface is in the three cases

$$r_1 - r_0 = kb [1 + \varepsilon (1 + \eta) (\frac{1}{3} - \sin^2 \varphi)],$$

$$r_2 - r_0 = kb [1 + \varepsilon (\frac{1}{3} - \sin^2 \varphi)],$$

$$r_3 - r_0 = kb.$$

or, expressed in kilometers

$$r_1 - r_0 = 114 + 0.59 (\frac{1}{3} - \sin^2 \varphi),$$

$$r_2 - r_0 = 114 + 0.38 (\frac{1}{3} - \sin^2 \varphi)$$

$$r_3 - r_0 = 114.$$

The difference between the three definitions of the relation of the isostatic and the normal surfaces is thus considerable, especially in its effect on the compression. If the undisturbed surface of the different oceans are parts of one and the same equipotential surface, which is the geoid, and if at the same time the geoid does not differ more than a few tens of meters<sup>1)</sup> from an ellipsoid of revolution,

$$\Delta_b = 2.73 \quad \zeta_b = 1.52 \quad b_b \left( \frac{d\eta}{db} \right)_b = 1.63.$$

Further if we put  $\bar{b} = \frac{1}{2}(b_1 + b_0)$ , we have  $b_b - b_0 = 0.0177 \bar{b}$ , and consequently

$$\eta_0 = \eta_b - 0.0177 \times 1.63 = 0.530.$$

Taking now

$$\bar{\eta} = \frac{1}{2}(\eta_1 + \eta_0) = 0.546, \quad \bar{\varepsilon} = \frac{1}{2}(\varepsilon_1 + \varepsilon_0), \quad b_1 - b_0 = 0.0181 \bar{b},$$

We find

$$\varepsilon_1 - \varepsilon_0 = 0.0181 \bar{\eta} \cdot \bar{\varepsilon} = 0.0099 \bar{\varepsilon}.$$

Taking  $\bar{\varepsilon} = 0.00336$ , we have

$$\varepsilon_1 - \varepsilon_0 = 0.000033.$$

$$\varepsilon_1^{-1} - \varepsilon_0^{-1} = -2.9.$$

<sup>1)</sup> HELMERT, Geoid und Erdellipsoid, Zeitschr. der Ges. für Erdkunde, 1913, p. 17-34.

We cannot but take this latter as the normal surface. In that case the normal surface is very nearly an equipotential surface. The deviations of the geoid from the ellipsoid, or, which is the same thing, of the normal surface from the equipotential surface, are caused by the irregularities in the crust. They would be very much larger — in fact of the order of 1000 meters <sup>1)</sup> — if there were no isostatic compensation. If this point of view is adopted, then the normal surface can differ only very little from the “ideal” surface  $S_1$  as defined above. This will be assumed in what follows and no further reference will be made to the surfaces  $S_2$  and  $S_3$ . They were only discussed here to point out the necessity of precision in the definition of the relation between the isostatic and the normal surfaces.

3. Let  $A < B < C$  be the moments of inertia of a body about the axes of  $x, y, z$ . If the body rotates about the axis of  $z$  with the velocity  $\omega$ , then the outer surface, if it is an equipotential surface, is very nearly <sup>2)</sup> an ellipsoid whose principal axes are

$$b, \quad b(1 - \nu), \quad b(1 - \frac{1}{2}\nu)(1 - \epsilon).$$

If  $C - A$  and  $C - B$  are of the first order of smallness, and  $B - A$  of the second order, and if

$$J = \frac{3}{2} \frac{C - A - B}{2Mb^2}, \quad K = \frac{3}{2} \frac{B - A}{Mb^2},$$

then to the second order inclusive we have

$$\epsilon = J + \frac{1}{2} \varrho_1 + \epsilon^2 - \frac{1}{2} \epsilon \varrho_1 - \frac{3}{8} B_4 \dots \dots \dots (1)$$

$$\nu = K \dots \dots \dots (2)$$

The radius of the equator in longitude  $\lambda$  is  $b [1 - \nu \sin^2(\lambda - \lambda_0)]$ , if  $\lambda_0$  be the longitude of the axis of  $x$ . The compression of the meridian in longitude  $\lambda$  is thus  $\epsilon_\lambda = \epsilon + \frac{1}{2} \nu \cos 2(\lambda - \lambda_0)$ . Consequently  $\epsilon$  is the average compression of the meridians.

The value of  $\varrho_1$  in (1), viz.

$$\varrho_1 = \frac{\omega^2 r_1}{g'_1} = 0.0034496,$$

can be assumed to be exactly known. Further

$$B_4 = 0.0000029.$$

The equation (1) can thus be written

$$\epsilon = J + 0.0017287 \dots \dots \dots (1')$$

<sup>1)</sup> HELMERT, Höhere Geodäsie, II, p. 356.

<sup>2)</sup> The deviation from the ellipsoid is  $-\kappa b \sin^2 2\tau$ , where

$$\kappa = \frac{5}{8} \epsilon \varrho - \frac{7}{8} \epsilon^2 + \frac{3}{8} \frac{5}{2} B_4 = 0.0000051,$$

or  $b\kappa = 3.26$  meters. DARWIN, Scientific Papers, Vol. III, p. 102.

and the uncertainty in the numerical part is no more than a few units in the last decimal place given.

We also need the ratio

$$H = \frac{2C - A - B}{2C}.$$

For the ideal surface we have  $A_1 = B_1$ , and consequently

$$J_1 = \frac{3}{2} \frac{C_1 - A_1}{Mb_1^2}, \quad H_1 = \frac{C_1 - A_1}{C_1},$$

The true moments of inertia  $A$  and  $B$  may however be unequal. The ratio  $H$  can be determined with great accuracy from the constant of precession. The best modern determinations of this constant are (for 1850):

NEWCOMB (with corrections by HOUGH and HALM <sup>1)</sup> )	$p_1 = 50''.2486$
BOSS <sup>2)</sup> )	50.2511
DYSON and THACKERAY <sup>3)</sup> )	50.2503

We can thus take

$$p_1 = 50''.2500 \pm 0''.0010.$$

The lunisolar precession then becomes

$$p = 50''.373.$$

If now we take for the mass of the moon

$$\mu^{-1} = 81.50 \pm 0.07,$$

we find

$$H = 0.0032775 \pm 0.0000022.$$

The uncertainty is almost entirely due to  $\mu$  and not to  $p$ .

So far no assumptions have been made regarding the constitution of the earth. The theory of CLAIRAUT now leads to a determination of the ratio of  $J$  and  $H$ . We are thus able from  $H$  to compute  $J$ , and then  $\varepsilon$  from (1'). RADAU'S transformation of CLAIRAUT'S differential equation gives, to the first order of  $\varepsilon$  <sup>4)</sup>,

$$g = \frac{J}{H} = \frac{3}{2} \frac{C}{Mb^2} = 1 - \frac{2}{5} \frac{\sqrt{1+\eta}}{F_0} \dots \dots \dots (3)$$

where, also to the first order,  $\eta = 3 - 5 \frac{J}{\varepsilon}$ , and  $F_0$  is a certain

1) Monthly Notices, Vol. LXX, p. 587. See also: The Observatory, July 1913, p. 299.

2) Astronomical Journal, Vol. XXVI, p. 118.

3) Monthly Notices, Vol. LXV, p. 443.

4) This and other formulas of the theory of CLAIRAUT will be collected in the following paper.

mean value of a function  $F$  of  $\eta$  which differs very little from unity for values of  $\eta$  between 0 and  $\eta_1$ .

If the formula (3) is extended to the second order, it becomes very complicated. The range of  $H_0$  becomes wider, and therefore also of  $g$  and  $\varepsilon$ . The formula has been elaborated by DARWIN<sup>1)</sup> and VÉRONNET<sup>2)</sup>. The formulae given by these two authors are very different. DARWIN starts from a definite assumption regarding the constitution of the earth, and thus finds a definite value of  $\varepsilon$ . VÉRONNET introduces no assumptions, and consequently only gives limits for  $\varepsilon$ . Introducing the above value of  $H$  we find:

$$\text{DARWIN . . . . } \varepsilon^{-1} = 296.03.$$

$$\text{VÉRONNET . . . } 295.84 < \varepsilon^{-1} < 296.68.$$

The lower limit of  $\varepsilon^{-1}$  corresponds to the case of homogeneity, the upper limit to concentration of the whole mass in the centre. There can be no doubt, but that the actual distribution is nearer the first limit. The agreement of the results of DARWIN and VÉRONNET is thus complete, and we can adopt the value derived from DARWIN's formula. The m. e. of  $\varepsilon^{-1}$  due to the uncertainty of  $H$  is  $\pm 0.16$ . From the agreement of the results of DARWIN and VÉRONNET we may conclude that any probable hypothesis regarding the constitution of the earth differing from that of DARWIN would not cause in  $\varepsilon^{-1}$  a difference exceeding say  $\pm 0.10$ . We thus estimate the total uncertainty of  $\varepsilon^{-1}$  at  $\pm 0.19$ .

4. However, the value of  $H$  used above is the ratio of the *true* moments of inertia. The equation (3) on the other hand is only applicable to the *ideal* surface. We must thus try to derive the values of  $J_1$  and  $H_1$  for the ideal surface from the true values  $J$  and  $H$ , and at the same time determine the difference  $\varepsilon - \varepsilon_1$  of the compressions of the normal and the ideal surfaces. This will be done on the basis of the hypothesis of isostasy.

The normal surface is the ellipsoid best fitting the geoid. The potential on the geoid depends on the true moments of inertia. The compressions  $\nu$  and  $\varepsilon$  of the normal surface are therefore derived by the equations (1) or (1') and (2) by using the true values of  $J$  and  $K$ . The equation (1) or (1') also applies to the ideal surface. Consequently

1) The theory of the figure of the earth to the second order of small quantities. Scientific Papers, Vol. III, p. 78--118.

2) Rotation de l'ellipsoïde hétérogène et figure exacte de la Terre. Journal des Math. 1912, 4me fascicule.

$$\varepsilon - \varepsilon_1 = J - J_1.$$

The change in  $H$  due to the change in  $C$  in the denominator is very small (of the order of  $1/300$ ) compared with the effect of the change in the numerator. Consequently

$$J - J_1 = g (H - H_1).$$

and

$$\varepsilon - \varepsilon_1 = g (H - H_1) = 0.502 (H - H_1). \quad \dots \quad (4)$$

The part contributed towards the moments of inertia by an element of mass  $m$  at latitude  $\varphi$ , longitude  $\lambda$ , and distance from the centre  $r$  is

$$\begin{aligned} dC &= mr^2 \cos^2 \varphi, \\ dA &= mr^2 [1 - \cos^2 \varphi \cos^2 (\lambda - \lambda_0)], \\ dB &= mr^2 [1 - \cos^2 \varphi \sin^2 (\lambda - \lambda_0)], \end{aligned}$$

from which

$$\begin{aligned} d [C - \frac{1}{2} (A + B)] &= mr^2 (1 - 3 \sin^2 \varphi) \\ d [B - A] &= mr^2 \cos^2 \varphi \cos 2 (\lambda - \lambda_0). \end{aligned}$$

If now over a surface element  $\omega$  of the ideal surface the height of the continent is  $h_1$  and the mean density  $\Delta$ , then the mass is  $m = \omega \Delta h_1$ . If  $Z_1$  is the depth of the isostatic surface below the ideal surface, the defect of density needed to compensate this mass, if equally distributed over the whole depth, is  $\sigma = \Delta \frac{h_1}{Z_1}$ . The change in  $\Sigma mr^2$  produced by the continent and its isostatic compensation then is, if  $r_1$  be the radius vector of the ideal surface :

$$d(\Sigma mr^2) = \int_{r_1}^{r_1+h_1} \Delta \omega x^2 dx - \int_{r_1-Z_1}^{r_1} \sigma \omega x^2 dx = \Delta \omega h_1 (Z + h_1) (r_1 - \frac{1}{3} Z_1 + \frac{1}{3} h_1), \quad \dots \quad (5)$$

Similarly for an oceanic element, let  $d_1$  be the depth of the bottom of the ocean below the ideal surface and  $\Delta'$  the difference of density between the water and the mean density of the crust. The compensating excess of density below the sea then becomes  $\sigma' = \frac{d_1}{Z_1 - d_1} \Delta'$ ,

and the change in  $\Sigma mr^2$  is

$$d'(\Sigma mr^2) = \Delta' \omega d_1 [(-Z_1 + 2d_1) r_1 + \frac{1}{3} Z_1^2 + \frac{1}{3} Z_1 d_1]. \quad \dots \quad (6)$$

It has been found sufficiently exact for our purpose instead of (5) and (6) to use the approximate formulæ

$$\begin{aligned} d(\Sigma mr^2) &= q \cdot h_1 \quad \dots \quad (5') \\ d'(\Sigma mr^2) &= -0.57 q \cdot d_1 \quad \dots \quad (6') \end{aligned}$$

The height  $h_1$  above the ideal surface is the sum of the height  $h$  above the normal surface and the height  $h'$  of the normal above the ideal surface. This latter is

$$h' = (\varepsilon - \varepsilon_1) b_1 \left( \frac{1}{3} - \sin^2 \varphi \right).$$

Taking  $Z_1 = 0.0179 r_1$ , and  $\Delta_1 = 2.70$ , and integrating over the whole surface we find for this part of  $H - H_1$ , using also (4):

$$\sigma' H = 0.023 (\varepsilon - \varepsilon_1) = 0.012 (H - H_1) \quad . \quad . \quad . \quad (7)$$

The principal part of  $H - H_1$  is due to the deviation of the actual surface from the normal surface. This has been computed by (5') and (6'), replacing  $h_1$  and  $d_1$  by  $h$  and  $d$  respectively. The value of the constant  $q$  depends on  $Z$  and on the units used. I have adopted  $\Delta = 2.70$ ,  $\Delta' = 1.70^1$ ,  $Z = 114$  km.

The surface of the earth was divided into compartments of about 100 square degrees. For each compartment the value of

$$Q = q\omega (\alpha_1 h - 0.57 \alpha_2 d).$$

was computed, where  $\alpha_1$  and  $\alpha_2$  are the fractions of the compartment covered by land and by sea respectively (so that  $\alpha_1 + \alpha_2 = 1$ ). Further

$$P = Q (1 - 3 \sin^2 \varphi)$$

$$R = Q \cos^2 \varphi \cos 2\lambda$$

$$S = Q \cos^2 \varphi \sin 2\lambda.$$

The units had been so chosen that

$$\sigma \frac{2C - A - B}{2C} = 10^{-7} \Sigma P$$

$$\sigma \frac{B - A}{C} = 10^{-7} \{ \Sigma R \cdot \cos 2\lambda_0 + \Sigma S \cdot \sin 2\lambda_0 \},$$

The longitude  $\lambda_0$  is determined by

$$\Sigma S \cos 2\lambda_0 - \Sigma R \sin 2\lambda_0 = 0.$$

I found the following results. (See table p. 1304).

We find thus

$$\sigma \frac{2C - A - B}{2C} = - 0.00000512$$

$$\sigma \frac{B - A}{C} = + 0.00000205,$$

and the axis of minimum moment of inertia ( $A$ ) is situated in the longitude

$$\lambda_0 = 86.95 \text{ West of Greenwich.}$$

This computation, of course, is rather rough. It would perhaps be worth while to repeat it with greater care. The small influence of the continents, especially of Asia, is somewhat surprising. This

<sup>1</sup>) The normal density of the crust in the upper few kilometers below the normal surface was thus taken to be 2.73, and the density of the land projecting above that surface 2.70.

Parts of the world.	$\Sigma P$	$\Sigma R$	$\Sigma S$
1. North Polar Area	+ 2.44	- 0.02	+ 0.03
2. Europe	- 0.83	+ 0.39	- 0.47
3. Asia	- 1.51	- 5.72	- 0.19
4. North-America	- 3.64	- 1.36	- 1.28
5. Northern Atlantic Ocean	- 5.00	- 0.23	- 11.36
6. South-America	+ 3.21	- 2.16	+ 2.56
7 Southern Atlantic Ocean	- 0.45	- 11.65	- 6.36
8. Africa	+ 3.55	+ 2.22	- 3.29
9. Indian Ocean	- 2.58	+ 15.11	+ 7.09
10. Indian Archipelago and Australia	- 2.14	+ 1.12	- 1.57
11. Pacific Ocean	- 29.97	- 17.96	+ 17.97
12. South Polar Area	- 14.27	- 0.03	+ 0.02

is due to the remarkable fact that the great mountainous regions of the earth (Himalaya, the Alps, Rocky Mountains, the higher part of South Africa) are situated on or near the neutral latitude of which the *sine* is  $\sqrt{1/3}$  [ $\varphi = 35^{\circ}.3$ ].

The value of  $\delta H$  found here is not yet exact, for if the crust were built according to the theory of CLAIRAUT it would consist of a solid crust covered by an ocean of a mean depth of about 2.4 km. In the above computation this ocean has been taken of the density 2.73 instead of 1.03. To remedy this we must apply a correction, which by the theory of CLAIRAUT is

$$\delta_1 (C-A) = \frac{8}{15} \pi \int_{b_1-2.4}^{b_1} \Delta' \frac{d}{d\beta} (\beta^5 \varepsilon) d\beta = \frac{8}{15} \pi \cdot 2.4 (5 + \eta) b^4 \varepsilon.$$

This gives

$$\delta_1 H = + 0.00000213. {}^1)$$

The bottom and the surface of this ocean would be ellipsoids of revolution, the neglect has therefore no effect on the value of  $B-A$ .

There now remains

$$\delta H = - 0.00000299.$$

<sup>1)</sup> There is an error of computation in this number. It should be  $+0.00000260$ . The final value then becomes  $\varepsilon^{-1} = 295.98$ . The difference from the value in the text is negligible. (Added in the English translation.)

Adding this to  $\sigma'H$  as given by (7) we have altogether

$$H - H_1 = -0.00000299 + 0.012(H - H_1)$$

or

$$H - H_1 = -0.0000031,$$

Then we find by (4)

$$\varepsilon - \varepsilon_1 = -0.0000016$$

$$\varepsilon^{-1} - \varepsilon_1^{-1} = +0.14.$$

From

$$H = 0.0032775$$

we find thus

$$H_1 = 0.0032806.$$

DARWIN's equation then gives

$$\varepsilon_1^{-1} = 295.82,$$

and from the equation of VÉRONNET we find

$$295.62 < \varepsilon_1^{-1} < 296.46.$$

It has already been mentioned that DARWIN's value may be assumed to be very near the truth. Adopting this and adding the value of  $\varepsilon^{-1} - \varepsilon_1^{-1}$ , which has been found above, we have<sup>1)</sup>

$$\varepsilon^{-1} = 295.96.$$

It is very difficult to estimate the uncertainty of the correction  $H - H_1$ , since it depends not only on the correctness of the data used, but also, and probably for the greater part, on the exactness of the hypothesis that the compensating defect or excess of density is distributed equally over the whole depth  $Z$ . The whole correction to  $\varepsilon^{-1}$  however only amounts to 0.07, and its uncertainty is almost certainly overestimated if we take it equal to the whole amount,  $\pm 0.07$ . Combining this with the m.e.  $\pm 0.19$  due to the uncertainty of  $H$ , and of DARWIN's hypothesis, the total uncertainty of  $\varepsilon^{-1}$  is found to be  $\pm 0.20$ .

The greater part of this is due to the uncertainty of  $H$ , and this is wholly due to that of the adopted value of the moon's mass. Consequently, in order to improve our knowledge of  $\varepsilon$  we must determine  $\mu$ , which is found from the lunar inequality of the sun's longitude and the solar parallax. A correction of  $+0.05$  to the adopted value of  $\mu^{-1}$  would give  $-0.10$  in  $\varepsilon^{-1}$ .

For the ideal surface  $B_1 = A_1$ , or  $K_1 = 0$ . Therefore for the normal surface

$$v = K = \frac{3}{2} \frac{C}{Mb^2} \cdot \frac{B-A}{C} = 0.00000103.$$

The longest radius of the equator, in the longitude  $86^\circ.5$  is thus

<sup>1)</sup> See note on p. 1304.

6.4 meters longer than the shortest radius. The compression of the meridian  $\epsilon_\lambda$  varies between  $\epsilon + \frac{1}{2}v$  and  $\epsilon - \frac{1}{2}r$ . For central Europe,  $\lambda = -30^\circ$ , we find :

$$(\epsilon_E)^{-1} = 295.98$$

and for North-America,  $\lambda = 100^\circ$

$$(\epsilon_A)^{-1} = 295.92.$$

5. The methods mostly used for the determination of the compression of the earth are :

- I. From geodetic measures,
- II. From the intensity of gravity,
- III. From the moon's parallax,
- IV. From the lunar theory.

By the first method the geodetic measures made in the United States of America give

$$\epsilon^{-1} = 297.0 \pm 1.2 \quad . . . . . (I)$$

This agrees within the limits of the mean error with the value 296.0 found above.

From a great number of determinations of the intensity of gravity HELMERT derived

$$\epsilon^{-1} = 298.3 \pm 1.1 \quad . . . . . (II)$$

This result agrees with the final result from the American determinations, viz.:

$$\epsilon^{-1} = 298.4 \pm 1.5 \quad . . . . . (II')$$

In judging the value of these results it must be remembered that both the direction (method I) and the intensity (method II) of gravity, before they are used for the determination of the figure of the geoid, or of an ellipsoid of reference, need certain corrections, which have been applied by different investigators more or less in agreement with the hypothesis of isostasy. All investigators however use approximate formulas, and it is not clear which of the definitions, treated in art. 2 above, has been adopted. The American investigators take a constant depth below the *actual* surface of the earth (under the sea even below the *bottom*). HELMERT uses the reduction as in free air<sup>1)</sup>, thus assuming that the isostatic compensation is complete.

Now it is of course impossible from the observations to decide between the three cases of art. 2, and also the corrections computed under the three assumptions will be very nearly equal. But small

<sup>1)</sup> The American observations reduced by the free air method give instead of (II')  $\epsilon^{-1} = 292.1 \pm 1.7$ . See BOWIE, Effect of topography and isostatic compensation upon the intensity of Gravity, second paper, p. 26.

differences in the radius of curvature, or in the values of  $g$ , have a large influence on the compression, and it seems not impossible that the resulting value of  $\epsilon$  has been influenced by inaccuracies in the reductions. Discussing the large difference between the compressions found by BESSEL ( $\epsilon^{-1} = 299.15$ ) and CLARKE (293.47) partly from the same observations, HELMERT<sup>1)</sup> asserts that this difference can be fully explained by a difference of a few meters in the adopted height of the geoid over the normal surface. If this is so, we can expect that considerably larger differences of the isostatic reduction will lead to similar effects<sup>2)</sup>.

For these reasons it appears to me that the agreement of the three values (I), (II) and (II') can only be accidental. It is not at all certain a priori whether they refer to the same normal surface, and their uncertainty undoubtedly is considerably larger than would be inferred from the mean errors.<sup>3)</sup>

From the lunar parallax we found in the preceding paper

$$\epsilon^{-1} = 293.4 \dots \dots \dots \text{(III)}$$

We also showed that the value 296.0 cannot be said to be excluded by the observations.

The lunar theory gives  $J$ , from which  $\epsilon$  is found by the equation (1'). The principal term, which is commonly used for the deter-

<sup>1)</sup> Geoid und Erdellipsoid, l.c. p. 18.

<sup>2)</sup> The values of  $\epsilon$  derived from the American determinations by different methods of reduction (and different combinations of stations) are widely divergent. Thus e.g. from the observations in the United States and in Alaska by the isostatic method  $300.4 \pm 0.7$  and by the free air method  $291.2 \pm 0.7$ . See BOWIE, l.c. p. 26. The former of these should properly be quoted instead of (II') as the final result from the American determinations.

<sup>3)</sup> HELMERT's formula of 1901, from which (II) is derived, reduced to the Potsdam system, is

$$g = 9.78030 [1 + 0.005302 \sin^2 \varphi - 0.000007 \sin^2 2 \varphi] \dots \text{(a)}$$

With the compression  $\epsilon^{-1} = 296.0$ , and a constant correction of  $+0.00011$  this becomes

$$g = 9.78041 [1 + 0.0052764 \sin^2 \varphi - 0.0000074 \sin^2 2 \varphi] \dots \text{(b)}$$

The residuals of these two formulas for different zones of latitude are as follows, expressed in units of 0.00001 :

Zone	5°	15°	25°	35°	45°	55°	65°	75°
(a)	+7	0	-20	+6	+6	+11	-7	-3
(b)	-4	-9	-4	+3	+8	+17	+3	+10

The m. e. of each of these residuals is  $\pm 11$ . The residuals  $\beta$  naturally are somewhat systematic, but they are not larger than (a), and can very well be due to errors of observation or inaccuracies in the reductions. A new discussion on the basis of the theory of isostasy, and including the valuable material, which has become available since 1900, is very desirable. [Note added in the English translation].

mination of  $J$ , is a periodic term in the latitude, whose period is one month and whose coefficient is, by BROWN's theory: <sup>1)</sup>

$$B = - [3.7046] J - 0''.017.$$

From the observations BROWN finds <sup>2)</sup>

$$B = - 8''.19 \pm 0''.06 - [0''.40 \pm 0''.20] . T,$$

where  $T$  is the time expressed in centuries and counted from 1850.0. If we take the mean epoch of the observations, i.e. about 1875, we find <sup>3)</sup>  $J = 0.001633$ , and consequently

$$\epsilon^{-1} = 297.3 \pm 1.3. \quad . . . . . (IV)$$

It appears to me that this determination is not very reliable, chiefly on account of the large and uncertain coefficient of  $T$  in the observed value. BROWN proposes to use it not to determine  $\epsilon$ , but the inclination of the ecliptic and its secular variation. It seems very doubtful whether a correction to these elements thus determined would be a real improvement to our knowledge of them derived from other sources.

A great weight is attributed by BROWN to the determination of  $J$  from the motion of the perigee and the node. He finds

$$\epsilon^{-1} = 293.5 \pm 0.5 \quad . . . . . (IV')$$

In deriving the m.c. no account has been taken of the uncertainty of the theoretically determined part of these motions due to other causes. Among these other causes, however, is the figure of the moon, which is very imperfectly known. It will be shown in the following paper that it is very well possible to adopt such values for the quantities defining this figure, that the motions of the perigee and the node are in agreement with the value  $\epsilon^{-1} = 296.0$ . Smaller values of  $\epsilon$  however lead to very improbable conclusions regarding the constitution of the moon.

All our discussions thus lead to the conclusion that none of the other determinations is equal in accuracy to, or can throw a doubt on the determination from the constant of precession. We must therefore adopt as final value of the compression the result of this determination, viz:

$$\frac{1}{\epsilon} = 295.96 \pm 0.20.$$

<sup>1)</sup> Part V, Chapter XIII. (Memoirs of the R. A. S., Vol. LIX, Part I). On p. 80 the inequality is given as  $- 8''.355 \sin (w_1 + \psi)$ . This should be  $- 8''.553$ .

<sup>2)</sup> Monthly Notices, Vol. LXXIV, p. 564. BROWN gives probable errors, which I have changed to mean errors.

<sup>3)</sup> The theoretical value for 1875, corresponding to  $\epsilon^{-1} = 297.0$  is  $- 8''.312$ , the observed value is  $- 8''.28$ . The difference is therefore  $0 - C = + 0''.03$  and not  $- 0''.03$  as stated by BROWN, i.e. p. 565.

**Astronomy.** — “*The Motions of the Lunar Perigee and Node, and the Figure of the Moon.*” By Prof. W. DE SITTER.

1. The motions of the perigee and node of the moon have been derived from the observations by different investigators.

For the perigee the resulting sidereal motions are :

E. W. BROWN <sup>1)</sup>	146435".35
P. H. COWELL <sup>2)</sup>	.37
E. J. DE VOS VAN STEENWIJK <sup>3)</sup>	.29
NEWCOMB <sup>4)</sup>	.30

All these values have been reduced to the value 50".2500 of the constant of precession (see the preceding paper). The first three depend on meridian observations. The agreement between COWELL and BROWN is excellent, but the result of DE VOS deviates rather more than can be explained by the mean errors (which are about  $\pm 0''.02$  for each result). It is, however, in perfect agreement with the value derived by NEWCOMB from the discussion of occultations.

The theoretical motion due to other causes than the figures of the earth and moon is by BROWN's theory :

$$146428''.77.$$

There thus remains for these two causes

I. BROWN—COWELL	$d\tilde{\omega} = + 6''.59$
II. NEWCOMB—DE VOS	$d\tilde{\omega} = + 6''.53.$

For the node the results derived by NEWCOMB<sup>4)</sup> and BROWN<sup>5)</sup> are in perfect agreement. They both find

$$- 69679''.44^5$$

The theoretical value, as above, is

$$- 69673''.22.$$

The part due to the figures of the earth and moon is thus

$$d\Omega = - 6''.22^5.$$

The mean errors of both values of  $d\tilde{\omega}$  and of  $d\Omega$ , so far as it is due to the observations, is  $\pm 0''.02$ . The theoretical value, however, in both cases is the sum of a large number of terms, each

<sup>1)</sup> Monthly Notices, Vol. LXXIV, p. 419.

<sup>2)</sup> Monthly Notices, Vol. LXXV, p. 275.

<sup>3)</sup> These Proceedings, Vol. XVI, p. 891.

<sup>4)</sup> Researches on the motion of the Moon. (Second paper), p. 224. The corrections indicated by BROWN, M.N. Vol. LXXIV, pp. 420 and 562 have been applied.

<sup>5)</sup> Monthly Notices, Vol. LXXIV, p. 563.

of which was computed to two decimals only, and may thus be 0".005 in error. The mean error of the sum can be assumed on this account to be about  $\pm 0".02$ . The mean error of the differences  $d\tilde{\omega}$  and  $d\Omega$  thus becomes  $\pm 0".03$ .

2. The terms due to the figure of the earth are, by BROWN'S theory, the factors being given as logarithms :

$$d\tilde{\omega} = [3.5907] J,$$

$$d\Omega = - [3.5620] J,$$

With  $\varepsilon^{-1} = 295.96 \pm 0.20$  (see the preceding paper), we have  $J = 0.0016502$ , from which

$$d\tilde{\omega} = 6".430 \pm 0".008,$$

$$d\Omega = - 6.019 \pm 0.007.$$

There thus remains for the figure of the moon

$$\begin{aligned} I \quad d\tilde{\omega} &= + 0".16 \pm 0".03, & d\Omega &= - 0".20^s \pm 0".03 \quad . \quad (1) \\ II \quad d\tilde{\omega} &= + 0.10 \pm 0.03, \end{aligned}$$

The values used in BROWN'S theory are

$$d\tilde{\omega} = + 0".03, \quad d\Omega = - 0".14.$$

The contradiction is apparently very great. It will be shown, however, that the values (1) can very well be ascribed to the figure of the moon. BROWN'S values depend only partially on actually determined constants, from which they are derived by means of the hypothesis that the ratio  $g = \frac{3}{2} \frac{C}{Mb^2}$  has the same value for the moon as for the earth. It will be seen below that the values (1) lead to a different value  $g'$ .

Let  $A'$ ,  $B'$ ,  $C'$  be the moments of inertia,  $M'$  the mass, and  $b'$  the largest radius of the moon. Further, in analogy with the notation used for the earth

$$J' = \frac{3}{2} \cdot \frac{2C' - A' - B'}{2M'b'^2} \quad ; \quad K' = \frac{3}{2} \cdot \frac{B' - A'}{M'b'^2}$$

Then the theoretical expressions for the motions of the perigee and the node are

$$\begin{aligned} d\tilde{\omega} &= + 390'' J' - 1027'' K', \\ d\Omega &= - 470 J' - 235 K'. \quad . \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

The coefficients are easily derived from BROWN'S theory, Chapter V, § 378 <sup>1)</sup>, where however  $\sigma b_2 = 6".57$ ,  $\sigma b_3 = - 6".15$ , must be

<sup>1)</sup> Memoirs R. Astr. Soc. Vol. LIX, Part I, p. 81.

substituted for  $+ 6''.41$  and  $- 6''.00$  respectively. The numerical coefficients in the next line of formulas then become

$$8''.62, - 45''.4 \text{ and } - 8''.07.$$

Then, discarding the assumption regarding  $C'/M: C'/E$ , and introducing  $J'$  and  $K'$ , the formulas (2) are easily derived.

Comparing (1) and (2) we find

<i>I</i>	<i>II</i>	$\frac{1}{2}(I+II)$	<i>m.e.</i>	
$J' = 0.000435$	$0.000410$	$0.000422$	$\pm 0.000055$	} (3)
$K' = 0.000069$	$0.000057$	$0.000033$	$\pm 0.000032$	

3. The ratios

$$\alpha = \frac{C'-B'}{A'} \quad , \quad \beta = \frac{C'-A'}{B'} \quad , \quad \gamma = \frac{B'-A'}{C'}$$

are, in the case of the moon, so small that we may neglect the difference of the numerators, and take  $\beta = \alpha + \gamma$ .

These ratios appear in the theory of the libration of the moon <sup>1)</sup>, where they are analogous to  $H = \frac{C-A}{C}$  in the theory of precession

and nutation. Generally  $\beta$  and  $f = \frac{\alpha}{\beta}$  are introduced as unknown quantities to be determined from the observations. The constant  $\beta$  is derived with great accuracy from the mean inclination of the moon's equator on the ecliptic. The equation determining this mean inclination  $\theta_0$  as a function of  $\beta$  is given by TISSERAND, Vol. II, p. 472, and also, more exactly, by HAYN, Selenographische Koördinaten, I<sup>2)</sup>, p. 900, with a further addition on p. 909. The values of  $\theta_0$  derived by different investigators are:

FRANZ,	from observations by SCHLÜTER	$\theta_0 = 1^\circ 31' 22''.1 \pm 7''.3$
STRATTON,	,, ,, ,, ,,	1 29 37 $\pm 71$
HAYN . . . . .		1 32 6 $\pm 15$

I adopt

$$\theta_0 = 1^\circ 31' 40'' \pm 20''.$$

Introducing this into HAYN's equation, I find

$$\beta(1 + 0.0047 f) = 0.0006286 \pm .0000022.$$

For  $f = 0$  this gives  $\beta = 0.0006286$ ,

and for  $f = 1$  . . . . .  $\beta = 0.0006257$ .

Now we have from (3)

$$J' + \frac{1}{2} K' = 0.000439 \pm .000066$$

1) See e.g. TISSERAND, Mécanique céleste, Tome II, Chapter XXVIII.

2) Abh. der K. Sächs. Ges. der Wiss. Band XXVII, Nr. IX, 1902.

Referring to the definitions given above we have

$$J' + \frac{1}{2} K' = g' \cdot \beta$$

Taking now

$$\beta = 0.000626 \pm .000002,$$

we find

$$g' = 0.70 \pm 0.11,$$

which differs considerably from the value for the earth ( $g = 0.502$ ).

If  $f$  is brought into evidence in the expressions for  $d\tilde{\omega}$  and  $d\tilde{\Omega}$  we have,

$$\begin{aligned} d\tilde{\omega} &= [-832'' + 1222'' f] (J' + \frac{1}{2} K'), \\ d\tilde{\Omega} &= -470'' (J' + \frac{1}{2} K'). \end{aligned}$$

From  $d\tilde{\Omega}$  we find, of course, the value of  $J' + \frac{1}{2} K'$  stated above, and then from  $d\tilde{\omega}$ :

$$\left. \begin{array}{llll} I & II & \frac{1}{2}(I + II) & m. e. \\ f = 0.98 & 0.87 & 0.92^5 & \pm 0.06^5 \end{array} \right\} \quad (5)$$

Generally  $f$  is determined from the coefficients of certain terms in the libration in longitude, which depend on  $\gamma^1$ , and of which the largest are, for  $f = \frac{1}{2}$ ,  $-156'' \sin S$  and  $+22'' \sin M$ , where  $S$  and  $M$  are the mean anomalies of the sun and moon respectively. The geocentric amplitudes of these oscillations are  $1''.4$  and  $0''.2$  respectively. It is hardly surprising that the determinations of such small quantities by different observers are not very accordant. The results are

$$\begin{array}{ll} \text{FRANZ} & f = 0.48777 \pm 0.0278 \\ \text{STRATTON} & 0.50 \pm 0.03 \\ \text{HAYN} & 0.75 \pm 0.04. \end{array}$$

The results of FRANZ and STRATTON are both derived from the observations by SCHLÜTER. The results of the different observers are very discordant amongst themselves as well as with the value (5). It seems certain that the mean errors of the values derived from the observations of the libration are no true measure of the real accuracy. The true value of  $f$  is certainly much nearer to unity than to  $\frac{1}{2}$ . The value found by SCHLÜTER and others for the coefficient of the principal term of the libration in longitude must then be due to systematic errors in the observations with a period of a year<sup>2</sup>).

<sup>1</sup>) It would thus be more natural to take as unknown  $\frac{\gamma}{\beta} = 1 - f$ . All writers have however expressed their results in terms of  $f$ .

<sup>2</sup>) See also HAYN, Selenographische Koordinaten II, p. 135—136. He there finds  $f = 0.85 \pm 0.07$  and explains how the smaller values found by FRANZ and HARTWIG (0.47) can be due to errors in the adopted radius-vector of MÖSTING A which, through optical libration, give rise to a spurious oscillation of yearly period, if the observations are made near the time of full moon.

We may remark that  $f$  cannot exceed unity. A value of  $f$  larger than 1 would mean that the moment of inertia about the axis pointing to the earth was larger than about the axis which is tangent to the orbit, and this would be an unstable state.

4. The theory of CLAIRAUT would lead to values of  $J'$ ,  $\beta$ ,  $f$  and  $g'$ , which are absolutely in contradiction with those found above from the observations.

Although the development of the theory is well known, and also its application to an ellipsoid with three unequal axes introduces no new principles, it is perhaps not devoid of interest to collect the different formulas into a concise summary.

The forces acting on the moon are: its own gravitational attraction, the attraction of the earth, and the centrifugal force. Take a system of coordinate axes, with its origin in the centre of gravity of the moon and the axis of  $Z$  along the axis of rotation. We can with sufficient approximation suppose the earth to be situated on the axis of  $X$  at a constant distance  $R$  from the origin.

The equipotential surfaces are approximately ellipsoids of which the principal axes are situated along the coordinate axes, and have the lengths

$$\beta, \quad \beta(1 - v), \quad \beta(1 - \sigma)$$

Further the equipotential surfaces are also surfaces of equal density. The density at any point is denoted by  $\Delta$  and the mean density within any equipotential surface by  $D$ . We have thus

$$D = \frac{1}{\beta^3(1-\sigma)(1-r)} \int_0^{\beta} \Delta \frac{d}{d\beta} [\beta^3(1-\sigma)(1-r)] d\beta.$$

As we will only develop the theory to the first order of  $r$  and  $\sigma$  inclusive, we require  $D$  only to the order zero, thus

$$D = \frac{3}{\beta^3} \int_0^{\beta} \Delta \beta^2 d\beta.$$

Further we introduce the integrals

$$S = \frac{1}{\beta^5} \int_0^{\beta} \Delta \frac{d}{d\beta} (\beta^5 \sigma) d\beta, \quad T = \int_{\frac{\beta}{2}}^{\beta} \Delta \frac{d\sigma}{d\beta} d\beta,$$

$$P = \frac{1}{\beta^5} \int_0^{\beta} \Delta \frac{d}{d\beta} (\beta^5 r) d\beta, \quad Q = \int_{\frac{\beta}{2}}^{\beta} \Delta \frac{dr}{d\beta} d\beta.$$

If then  $r, \varphi, \lambda$  are the polar coordinates of any point, the potential  $V_1$  at that point due to the attraction of the moon is given by <sup>1)</sup>

$$\frac{3}{4\pi f} V_1 = \frac{D\beta^3}{r} + \left(\frac{1}{5} - \frac{3}{5} \sin^2 \varphi\right) \left[\frac{\beta^5}{r^3} S + r^2 T\right] +$$

$$+ \left(\frac{1}{5} - \frac{3}{5}\right) \cos^2 \varphi \sin^2 \lambda \left[\frac{\beta^6}{r^3} P + r^2 Q\right].$$

If  $\omega$  be the velocity of rotation, and if we put

$$Q = \frac{3\omega^2}{4\pi f D},$$

then the potential of the centrifugal force is

$$\frac{3}{4\pi f} V_2 = \frac{1}{2} D Q r^2 \cos^2 \varphi.$$

Further if  $M$  be the mass of the earth, and

$$z = \frac{3M}{4\pi R^3 D},$$

the potential of the attraction of the earth is

$$\frac{3}{4\pi f} V_3 = Dz \left[1 - \frac{3}{5} \sin^2 \varphi - \frac{3}{2} \cos^2 \varphi \sin^2 \lambda\right].$$

Along an equipotential surface the sum  $V = V_1 + V_2 + V_3$  must be constant. If we are content with the first order of  $\sigma$  and  $v$  we can also take  $r = \beta$  in the factors of  $S, T, P, Q, \varphi$  and  $z$ . The equation to the equipotential surface then becomes, if  $a$  is a constant:

$$\frac{r}{a} = D \left(1 + \frac{1}{3} Q\right) + \left(\frac{1}{2} - \frac{3}{5} \sin^2 \varphi\right) \left[\frac{2}{5} (S + T) + \frac{1}{3} DQ + Dz\right]$$

$$+ \left(\frac{1}{2} - \frac{3}{5} \cos^2 \varphi \sin^2 \lambda\right) \left[\frac{2}{5} (P + Q) + Dz\right].$$

The equation of the ellipsoid is

$$r = \beta \{1 - \sigma \sin^2 \varphi - v \cos^2 \varphi \sin^2 \lambda\}.$$

Comparing the coefficients of  $\sin^2 \varphi$  and  $\cos^2 \varphi \sin^2 \lambda$ , we find

$$\left. \begin{aligned} D\sigma &= \frac{3}{5} (S + T) + \frac{1}{2} DQ + \frac{3}{2} Dz, \\ Dv &= \frac{3}{5} (P + Q) + \frac{3}{2} Dz. \end{aligned} \right\} \dots \dots \dots (6)$$

The quantities referring to the outer surface will be distinguished by the suffix 1. We then have

$$M' = \frac{4}{3} \pi D_1 b'^3,$$

$$C' - A' = \frac{8}{15} \pi S_1 b'^5, \quad B' - A' = \frac{8}{15} \pi P_1 b'^5,$$

$$T_1 = 0, \quad Q_1 = 0.$$

<sup>1)</sup> The constant of the gravitation  $f$  in this formula of course is a different thing from the ratio  $f$ , which has been defined above.

Consequently for the outer surface we have

$$\left. \begin{aligned} \sigma_1 &= \frac{3}{2} \frac{C' - A'}{M'b'^2} + \frac{1}{2} Q_1 + \frac{3}{2} \alpha_1, \\ v_1 &= \frac{3}{2} \frac{B' - A'}{M'b'^2} + \frac{3}{2} \alpha_1. \end{aligned} \right\} \dots \dots \dots (7)$$

Putting now

$$\epsilon_1 = \sigma_1 - \frac{1}{2} v_1,$$

so that  $\epsilon_1$  is the mean compression of the meridians, we find

$$\left. \begin{aligned} \epsilon_1 &= J' + \frac{1}{2} Q_1, \\ v_1 &= K' + \frac{3}{2} \alpha_1 \end{aligned} \right\} \dots \dots \dots (8)$$

5. We now put

$$\eta = \frac{\beta}{\sigma} \cdot \frac{d\sigma}{d\beta}, \quad \theta = \frac{\beta}{v} \cdot \frac{dv}{d\beta}, \quad \zeta = -\frac{\beta}{D} \cdot \frac{dD}{d\beta}.$$

From the definition of  $D$  we find easily

$$\zeta = 3 \left( 1 - \frac{\Delta}{D} \right).$$

If now the assumption is made that the density never increases from the centre outwards <sup>1)</sup>, we have always  $1 \geq \frac{\Delta}{D} \geq 0$ , or

$$0 \leq \zeta < 3.$$

We now differentiate the equations (6). If the whole mass rotates as one solid body, then  $D\Omega$  is constant. Also  $D\alpha$  is a constant. We thus find easily

$$\left. \begin{aligned} \eta + 3 \left( \frac{S}{\sigma D} - 1 \right) &= 0 \\ \theta + 3 \left( \frac{P}{v D} - 1 \right) &= 0. \end{aligned} \right\} \dots \dots \dots (9)$$

We have thus

$$\beta^5 \sigma D (\zeta - \eta) = 3 (\beta^5 S - \beta^5 \Delta \sigma).$$

If for  $\beta^5 S$  we write  $\int_0^{\beta} \Delta \frac{d}{d\beta} (\beta^5 \sigma) d\beta$ , and integrate by parts, we find

<sup>1)</sup> It is not necessary to suppose that, for all values of  $\beta$ ,  $\frac{d\Delta}{d\beta} \leq 0$ . It is sufficient if

$$\int_0^{\beta} \beta^3 \frac{d\Delta}{d\beta} d\beta \leq 0 \quad \text{and} \quad \int_0^{\beta} \beta^5 \sigma \frac{d\Delta}{d\beta} d\beta \leq 0.$$

$$\beta^3 \sigma D(\zeta - \eta) = -3 \int_0^\beta \beta^5 \sigma \frac{d\Delta}{d\beta} d\beta.$$

Since  $\frac{d\Delta}{d\beta}$  is supposed never to be positive, the integral also cannot be positive, and we conclude

$$\zeta \geq \eta.$$

Similarly we find

$$\zeta \geq \theta.$$

Now differentiating (9) again, we find

$$\left. \begin{aligned} \beta \frac{d\eta}{d\beta} + 5\eta + \eta^2 - 2\zeta(1 + \eta) &= 0, \\ \theta \frac{d\theta}{d\beta} + 5\theta + \theta^2 - 2\zeta(1 + \theta) &= 0. \end{aligned} \right\} \dots \dots (10)$$

For  $\beta = 0$  we have  $\eta = \theta = 0$ . For small values of  $\beta$ ,  $\eta$  and  $\frac{d\eta}{d\beta}$  are therefore necessarily of the same sign. It follows from (10)

that this is only possible when  $\eta$  is positive;  $\eta$  and  $\frac{d\eta}{d\beta}$  thus begin by being both positive, and  $\eta$  cannot become negative without passing through zero. But, for values of  $\beta$  larger than zero, we find from (10) that, for  $\eta = 0$ ,  $\frac{d\eta}{d\beta}$  is positive. It follows that  $\eta$  can never become negative. The same reasoning holds for  $\theta$ . Collecting the different inequalities, which have been found we can write

$$\left. \begin{aligned} 0 \leq \eta \leq \zeta \leq 3, \\ 0 \leq \theta \leq \zeta \leq 3. \end{aligned} \right\} \dots \dots \dots (11)$$

From (10) we find

$$\beta \frac{d}{d\beta}(\eta - \theta) + 5(\eta - \theta) + (\eta + \theta)(\eta - \theta) - 2\zeta(\eta - \theta) = 0.$$

Putting now

$$y = \frac{\eta - \theta}{\beta},$$

we find

$$\beta \frac{dy}{d\beta} + [6 + \eta + \theta - 2\zeta]y = 0 \dots \dots \dots (12)$$

The factor in square brackets is necessarily positive, and is equal to 6 for  $\beta = 0$ . Putting thus

$$[6 + \eta + \theta - 2\zeta] = 6 + p\beta + q\beta^2 + \dots,$$

$$y = a + b\beta + c\beta^2 + \dots,$$

and substituting in (12), we can successively determine the constants  $a, b, c \dots$ . We find that all these coefficients are zero. Consequently  $y=0$ , or

$$\eta = \theta.$$

This being so for small values of  $\beta$ , it remains true for all  $\beta$ , since  $\eta$  and  $\theta$  satisfy the same differential equation.

Referring now to the various definitions given above, we conclude

$$\frac{v}{\sigma} = \frac{P}{S} = \frac{Q}{T} = \frac{P_1}{S_1} = \frac{B'-A'}{C'-A'} = \frac{\frac{3}{2}z_1}{\frac{3}{2}z_1 + \frac{1}{2}q_1} = 1 - f. \quad (13)$$

Now, since the velocity of rotation equals the mean motion in the orbit, we have by KEPLER'S third law, for the average value of  $R$ ,

$$R^3\omega^2 = AfM(1+\mu),$$

where the factor  $A$  is taken from the lunar theory. Therefore

$$\frac{Q}{z} = A(1+\mu) = 1.0095$$

We have thus from (13):

$$1 - f = 0.7482, \quad f = 0.2518.$$

We found above that for the actual moon the true value of  $f$  is probably very near unity. We must thus conclude that the distribution of mass within the moon is *not* approximately in accordance with the theory of CLAIRAUT.

6. Continuing however to trace the consequences of this theory, we now apply RADAU'S transformation of the differential equation (10) of CLAIRAUT. Since  $\theta = \eta$ , it is sufficient to treat the equation for  $\eta$ .

Put

$$\Phi = D\beta^5 \sqrt{1+\eta}.$$

Differentiating, and comparing with (10), we find

$$\frac{d\Phi}{d\beta} = 5D\beta^4 \cdot \frac{1 + \frac{1}{2}\eta - \frac{1}{10}\eta^2}{\sqrt{1+\eta}}$$

Now the function  $F = \frac{1 + \frac{1}{2}\eta - \frac{1}{10}\eta^2}{\sqrt{1+\eta}}$  is nearly constant for small

values of  $\eta$ , as will be seen from the following little table

$\eta = 0 \dots F = 1$	
$\frac{1}{3}$	1.00074 (maximum)
0.6	0.99928
1	0.98995
3	0.8

Therefore,  $F_0$  being a certain mean value of  $F$ , which will never differ much from unity, we have

$$D\beta^5 \sqrt{1+\eta} = \Phi = 5F_0 \int D\beta^4 d\beta, \dots (14)$$

Now the moment of inertia  $C'$  is given by

$$C' = \frac{8}{15} \pi \int_0^{b'} \Delta \frac{d}{d\beta} [\beta^5 (1-\sigma) (1-r)^2] d\beta$$

$$= \frac{8}{3} \pi \int_0^{b'} \Delta \beta^4 d\beta - (C' - A') - 2 (B' - A').$$

If in  $C'$  we neglect small quantities of the first order, we can take  $\Delta = D(1 - \frac{1}{3}\zeta) = D + \frac{1}{3}\beta \frac{dD}{d\beta}$ , and consequently

$$\int \Delta \beta^4 d\beta = \int D\beta^4 d\beta + \frac{1}{3} \int \beta^5 \frac{dD}{d\beta} d\beta.$$

Integrating the second integral in the right hand member by parts, and substituting in the value for  $C'$ , we find

$$C' = \frac{8}{9} \pi D_1 b'^5 - \frac{16}{9} \pi \int_0^{b'} D\beta^4 d\beta.$$

The integral is determined by (14). Introducing the mass  $M' = \frac{4}{3} \pi b'^3 D_1$  we find

$$g' = \frac{3}{2} \frac{C'}{M' b'^2} = 1 - \frac{8}{5} \frac{\sqrt{1+\eta_1}}{F_0} \dots (15)$$

Since  $0 \leq \eta_1 \leq 3$ , we have

$$\frac{3}{5} > g' > 0.$$

The upper limit corresponds to homogeneity, the lower limit to condensation of the whole mass in the centre.

We have found above

$$g' = 0.70 \pm 0.11. \dots (16)$$

The most probable value of  $g'$  is therefore outside the limits of CLAIRAUT, though the mean error does not entirely exclude a value near the upper limit. An excess of  $g'$  over the value for

homogeneity indicates that in the moon the density *increases* from the centre outwards. A small excess could of course be due to irregularities in the distribution of the mass. But, unless we are prepared to admit a considerable excess of density of the outer layers of the moon over the mean density, we are led to the conclusion that the true value of  $g'$  is certainly not larger and probably smaller than the value (16). Now this value was determined from the observed motion of the node combined with the adopted compression of the earth  $\varepsilon^{-1} = 296.0$ . For  $\varepsilon^{-1} = 297.0$  we should have found  $g' = 0.85$ , and HELMERT's value 298.3 gives  $g' = 1.02$ . Thus, if the observed motion of the node is accepted, any value of  $\varepsilon$  appreciably smaller than  $1/_{296}$  becomes very improbable.

7. From (7) and (9), combined with (11), we find easily

$$\begin{aligned} \frac{1}{2} \varrho_1 + \frac{3}{2} \varkappa_1 &\leq \sigma_1 \leq \frac{5}{4} \varrho_1 + \frac{1.5}{4} \varkappa_1, \\ \frac{3}{2} \varkappa_1 &\leq v_1 \leq \frac{1.5}{4} \varkappa_1. \end{aligned}$$

The numerical value is approximately

$$\varrho_1 = \varkappa_1 = 0.0000078.$$

Therefore

$$\begin{aligned} 0.0000156 &\leq \sigma_1 \leq 0.0000390 \\ 0.0000117 &\leq v_1 \leq 0.0000292. \end{aligned}$$

Take e.g.

$$\sigma_1 = 0.0000300, \quad v_1 = 0.0000225.$$

We then have from (6)

$$\frac{3}{2} \frac{C' - A'}{M'b'^2} = 0.0000144, \quad \frac{3}{2} \frac{B' - A'}{M'b'^2} = 0.0000108,$$

and consequently

$$J' = 0.000021 \quad , \quad K' = 0.000011.$$

For the limiting case of homogeneity, these values would become

$$J' = 0.000032 \quad , \quad K' = 0.000018.$$

The values derived from the motions of the perigee and the node were

$$J' = 0.000422 \pm .000055 \quad , \quad K' = 0.000033 \pm .000032.$$

Further we have from (9), with the above value of  $\sigma_1$ :

$$\eta_1 = 3 \left[ 1 - \frac{5}{2} \frac{C' - A'}{M'b'^2} \cdot \frac{1}{\sigma_1} \right] = 0.60.$$

Then from (15) taking  $F'_0 = 1$ , we find  $g' = 0.494$  and consequently:

$$\beta = \frac{C' - A'}{C'} = 0.000029.$$

For the case of homogeneity this would become

$$\beta = 0.000059.$$

The value derived from the mean inclination of the moon's equator was

$$\beta = 0.000626 \pm .000002.$$

Here again we find an enormous difference between the true values and the theory of CLAIRAUT.

8. The conclusion that the distribution of mass in the body of the moon is not in agreement with the theory of hydrostatic equilibrium, has already been reached by LAPLACE<sup>1)</sup>.

The mass constituting the crust of the earth is not in equilibrium either. But below the isostatic surface there is equilibrium. We are naturally led to assume that the depth of the isostatic surface is the depth at which the pressure of the outer layers becomes so large that the material of the earth behaves as a fluid and therefore necessarily is in equilibrium<sup>2)</sup>. To form an estimate of the pressure at the isostatic depth we can compute the pressure as it would be if the whole earth, including the crust, were in hydrostatic equilibrium. Then, treating the earth as a sphere, we have

$$p = \int_{b-Z}^b \Delta g \, dr,$$

where  $g$  is the acceleration of gravity. Now

$$g = \frac{fm}{r^2}, \quad m = \frac{4}{3} \pi r^3 D.$$

Therefore

$$p = \frac{4}{3} \pi f \int_{b-Z}^b \Delta \cdot D \cdot r \, dr$$

For the earth the interval of integration is relatively small, and we can take  $\Delta$  and  $D$  constant. Then  $D = D_1$  and very approximately  $\Delta = \frac{1}{2} D_1$ . Further if  $Z = kb$ , we find

$$p = \frac{2}{3} \pi f D_1^2 b^2 [k - \frac{1}{2} k^2].$$

1) Mécanique Céleste, Livre V, Chapitre II, § 18.

2) So far as constant, or slowly varying forces and stresses are concerned. The behaviour of the material with respect to sudden forces is of no importance for our argument.

The material out of which the moon is built up is probably not very different from that of the outer layers of the earth. We will therefore assume that it requires the same pressure to be fluid enough for the state of permanent equilibrium. If now on the moon the depth of the isostatic surface, if there be one, is  $Z' = k'b'$ , we have

$$p' = \frac{1}{3} \pi f \int_{b'-Z'}^{b'} \Delta' \cdot D' \cdot r dr.$$

Now we can put  $\Delta' \cdot D' = \alpha D_1'^2$ . If the moon were homogeneous, we should have  $\alpha = 1$ . If the density increases towards the centre, then at the outer surface  $\alpha < 1$ , and at the centre  $\alpha > 1$ . If  $\alpha_0$  be a certain mean value of  $\alpha$  over the interval of integration, we have

$$p' = \frac{1}{3} \pi f \alpha_0 D_1'^2 b'^2 [k' - \frac{1}{2} k'^2].$$

Now

$$b' = 0.272 b, \quad D_1' = 0.610 D_1.$$

Taking further  $k = 0.018$ , we find from the condition  $p' = p$

$$k' - \frac{1}{2} k'^2 = \frac{0.32}{\alpha_0}.$$

If we take  $\alpha_0 = 1$ , we find

$$k' = 0.40.$$

Most probably the true value of  $\alpha_0$  does not differ much from unity. The isostatic surface in the moon would thus be situated at a depth of about two fifths of the radius, and little more than one fifth of the total volume would be inclosed within it. Of course there can be no question of an isostatic compensation as there is in the earth. The differences of the moments of inertia are almost entirely determined by the irregularities in the "crust", which here contains by far the largest part of the mass, and the small central part has only very little influence.

This reasoning, of course, is not entirely rigorous, but it undoubtedly points out the true reason why the theory of CLAIRAUT, which in the case of the earth agrees so well with the actual facts, is not at all applicable to the moon.

**Physiology.** — “*The decoloration of fuchsin-solutions by amorphous carbon.*” By Dr. A. B. DROOGLEEVER FORTUYN. (Communicated by Prof. Dr. J. BOEKE).

Pulverized amorphous carbon has the faculty of decoloring solutions in water of several dyes, and the general explanation of this phenomenon is to be found in the fact that these pigments are absorbed by the carbon.

FREUNDLICH and LOSEV (*Zeitschrift für physikalische Chemie*, Bd. 59, 1907) discovered, that for Crystallviolett and Neufuchsin of the Höchster Farbwerke another explanation must be given. These two dyes are chlorides. If their solution in water is brought into contact with carbon, then the solution decolors. The dyes are however not absorbed as such, but they are decomposed into hydrochloric acid and color-base. The color-base is absorbed by the carbon, presumably in the form of a polymerisation product, which by means of alcohol can again be removed from the carbon. The hydrochloric acid remains behind in the fluid, and can be shown in the filtrate of the solution that has been decolorized by carbon by the opacity that occurs in it with silver-nitrate, and its acid reaction upon litmus.

In 1909 (*Zeitschr. f. Physik. Chemie*, Bd. 67) FREUNDLICH and NEUMANN wrote again about the absorption of Neufuchsin by carbon and corrected some inaccuracies in their former paper a.o. by remarking that the decolorized filtrate of Neufuchsin does not react acidly upon litmus. They proved that over 33% of the chlorine occurring in the Neufuchsin remains behind in the filtrate decolorized by carbon. They could not indicate with certainty the kation belonging to this anion Cl, but they are of opinion that these are partly H-ions, partly other ions resulting from inevitable contaminations of the carbon. According to them the thing absorbed by carbon from the Neufuchsin-solution may still be the color-base, but more probably it is a color-salt formed with contaminations of the carbon.

When repeating these experiments with “Crystallviolett” no deviations were found, but with “Neufuchsin” I observed a phenomenon being not in accordance with the view entertained by FREUNDLICH and his cooperators about the decoloration of solutions of this dye by carbon. This phenomenon consists in the fact, that a watery solution of  $\frac{1}{100}$  % Neufuchsin decolorized by carbon and filtrated from the carbon resumes its color for a great deal when it has been standing for a considerable time.

Not only Neufuchsin, but likewise the “fuchsine” of KIPP, Fuchsin

of GRÜBLER and Magentaroth of GRÜBLER, all very similar if not identical dyes, behave in the same manner.

This phenomenon is most easily, and in the shortest time observed, when so little carbon is added to the fuchsin-solution, that the color does not totally disappear, but a light-pink tinge remains. To control the change of the color a fuchsin-solution can be used that has been so far diluted, that, to the eye, it corresponds with the nearly decolorated solution. It will be seen that after the filtrage of the carbon, for which operation I used filters of SCHLEICHER and SCHÜLL, the color of the fluid becomes very distinctly deeper. That, after all, the carbon had really acted absorbingly, is proved by the deeply staining of aethylalcohol 96%, if the filtrated carbon is thrown into it. If we take carbon to an excess, it may easily occur, that the color is not seen returning in the decolorated solution, presumably because the concentration of the newly formed dye is insufficient.

The carbon originally used by me was gross-grained char-coal, which had not been carefully purified. Consequently the phenomenon could be attributed also to contaminations of the carbon. Therefore I purified the carbon according to the method likewise applied by FREUNDLICH and LOSEV by boiling it three times with 25% HCl and washing it with distilled water. Even after very long washing all the hydrochloric acid had not yet been removed, and carbon used in this condition prevented the return of the color of the decolorated fuchsin. But by adding ammonia to the carbon to which hydrochloric acid had been applied, and after washing it again, I could obtain carbon, the extract of which with distilled water contained no longer a vestige of chlorine. Only this carbon could be considered applicable to my purpose and with this carbon purified by me the phenomenon was regularly observed.

The fact that no heterogeneous substances could be the cause of the return of the color, was further confirmed by what follows. I obtained some samples of carbon from the „Kon. Pharmaceutische Handelsvereeniging” Amsterdam. If one washes one of these Carbo animal. depur. humida with distilled water, the filtrate reacts strongly acidly and it contains much chlorine. When this carbon was applied the phenomenon did not occur. Neither when Carbo sanguinis was used, the watery extract of which contained likewise chlorine but was alkaline. On the contrary the extract with water of Carbo ligni tiliae pulvis B. 50 as prescribed in the Dutch Pharmacopy Ed. IV was neutral, and no precipitation with silver-nitrate could be obtained. This carbon, which consequently can be regarded as sufficiently pure for my purpose admits the return of the color in an almost decolorated

fuchsin-solution. It is only not so handsome in its application as gross-grained carbon, because it is inclined to pass through the filter, and easily too much of it is added to the fuchsin-solution. If one adds carefully so little carbon, that the decoloration takes place slowly, e. g. in the course of a day, then one obtains here also easily a light-pink filtrate, which after some time becomes dark-red again.

Now the question rises how the return of the color in the almost wholly decolored fuchsin-solution can be explained. It is not for me to answer this question. This will have to be done by chemico-physical methods by a person who is sufficiently conversant with the theory of carbon-absorption. As an histologist I can do no more than publish the fact I have discovered, hoping that somebody else will further investigate its nature. Yet I have tried to find for myself an explanation of the case, and have come to a working hypothesis, which after all proved to be untenable, but made me discover some other facts that may have importance for the explanation I tried to find.

It was supposed, that in the almost decolored fuchsin-solution besides chlorine-ions or hydrochloric acid also uncolored dye kations or color-base would occur and this even in so great a quantity, that they must partly reconstruct the dye, causing likewise the color partly to return. This cannot be a pure ion-reaction for ion-reactions have a quick process, and the color returns only slowly, but in the color-base an alteration of structure may have taken place, a phenomenon of which examples are known.

Is it now possible to ascertain, that in an almost decolored fuchsin-solution more hydrochlorid acid and color-base occur than in an equally stained diluted fuchsin-solution which has never been in contact with carbon? Apparently it is.

Silver-nitrate occasions in the almost decolored fuchsin-solution a distinct opacity, but does not do so in the as deeply stained diluted solution. Consequently there are in the former case more Cl-ions than in the latter. In fact this is in conformity with what FREUNDLICH and LOSEV discovered.

Adding a few drops of acetic acid causes the color to return quickly and intensely in the almost decolored fuchsin-solution, whereas an as deeply stained diluted solution does not change its color by it. So, perhaps the acetic acid enables the color-base in the decolored solution to form very quickly a colored salt, for which there is of course no opportunity in the diluted solution.

I did not meet the phenomenon offered by fuchsin again in "Crystall-

violett" nor in any other dye experimented upon in this respect. Only „Säure-fuchsin", a dye which is no chloride and deviates considerably in composition from fuchsin showed something like it. It does not make any difference whether Säurefuchsin or Rubin S of GRÜBLER or Säurefuchsin S.M.P. of the Actien-Gesellschaft für Anilinfabrikation of Berlin is used for this purpose. I have never been able to state with certainty whether in a  $\frac{1}{50}$  ‰ Säure-fuchsin-solution being almost entirely decolored the color partly returns after the filtration of the carbon. But I have experienced, that in the almost decolored solution after the filtration and even after the lapse of some weeks the color can suddenly and very intensely be reproduced by acetic acid. It must be taken in consideration in this case, that acetic acid stains likewise a diluted Säure-fuchsin-solution which has never been in contact with carbon, somewhat more deeply, but by far not so much as the solution almost decolored by carbon.

I desist from suggesting an hypothesis for the explanation of the last mentioned phenomenon, and only hope, that the nature of what I have communicated here may, at some time or other, be explained and increase our knowledge of the theory of histological staining methods.

**Physiology.** — "*Phagocytes and respiratory centre.*"

*Their behaviour when acted upon by oxygen, carbonic acid, and fat-dissolving substances. Explanation of the excitement-stage in narcosis.*"<sup>1)</sup> By Prof. H. J. HAMBURGER.

(Communicated in the meeting of March 27, 1915).

*Introduction.*

In a former paper it was shown that Iodoform, even in extremely slight quantities can accelerate phagocytosis, to a considerable extent<sup>2)</sup>. We explained this action by assuming that this substance, after being dissolved in the lipid surface, softens the cells, thus facilitating the amoeboid motion.

If this view were correct, it might be expected that other substances which are soluble in lipoids, would act in the same way. This was indeed the case, without a single exception, with all the substances investigated, only not, as we found afterwards, with carbon sulphide. But in chloroform, chloralhydrate, ethylalcohol<sup>3)</sup>, butyric acid, propionic acid<sup>3)</sup>, benzole, turpentine, camphor, Peruvian balsam<sup>3)</sup> (cinamic

<sup>1)</sup> A detailed account will appear in the Internationale Zeitschrift für physikalisch-chemische Biologie. (ENGELMANN, Leipzig).

<sup>2)</sup> H. J. HAMBURGER, J. DE HAAN and F. BUBANOVIC, These Proceedings, March 25, 1911.

<sup>3)</sup> H. J. HAMBURGER and J. DE HAAN, Ibid, October 28, 1911.

acid) the same property became manifest, even when they were taken in very weak concentrations e.g. propionic acid 1 : 10.000.000, chloroform 1 : 5.000.000, chloralhydrate 1 : 20.000, alcohol 1 : 10.000, concentrations answering to the division-coefficients of these substances between oil and water.

In order to penetrate more deeply into the nature of this phenomenon, we asked ourselves if the entrance of these substances into the phagocytes resulted in a decreased viscosity or in a decreased surface-tension. But experiments in this direction made by BUBANOVIC in our laboratory<sup>1)</sup>, and after another and better method in that of Prof. ARRHENIUS<sup>2)</sup> at Stockholm, gave negative results; so did other experiments taken by myself later on. The object of these experiments was to investigate if the surface-tension of oil decreased under the influence of small quantities of chloroform and similar substances.

It must, however, be remembered that the lipoids of the cell-surface may not be considered identical with oil, so that it is not impossible that after all we have to deal with a decreased surface-tension. In order to ascertain if this is really the case the experiments of BUBANOVIC would have to be repeated with the lipoids of the white blood-corpuseles, but it is very difficult to obtain these substances in sufficient quantities. Perhaps in the future, methods may be available enabling us to determine these values with slighter quantities than are required at present.

But however this may be, as yet the experiments which aimed at establishing a modification in the viscosity or surface-tension under the influence of traces of fat-dissolving substances, have led to negative results.<sup>3)</sup>

Whilst looking forward to these researches with the lipoids of the blood-corpuseles or, better still, with naked protoplasm, we asked ourselves whether perhaps the acceleration of phagocytosis would not be accompanied by an increased oxygen-consumption, would perhaps even be caused by it.

This possibility had already been suggested by us before<sup>4)</sup>, and

1) F. BUBANOVIC, *Zeitschr. f. Chemie und Industrie der Kolloide*. **10** (1912), 178.

2) F. BUBANOVIC, *Middelanden f. K. Vetenskaps-Akademiens, Nobelinstitut N<sup>o</sup>. 17* (1911).

3) Later experiments however have shown, that small amounts of chloroform diminish the viscosity of Yolk. [Note added to the translation].

4) H. J. HAMBURGER: *Physikalisch-chemische Untersuchungen über Phagozyten. Ihre Bedeutung von allgemein biologischem und pathologischem Gesichtspunkt*. Wiesbaden, J. F. BERGMANN, 1912, S. 167.

had led HEGER and BARUCH to investigate the absorptive power of red blood-corpuses for chloroform in chloroform-narcosis. These investigators found indeed that during the chloroform-narcosis the oxygen-percentage of the red blood-corpuses is modified<sup>1)</sup>. It was found to have increased. Because less oxygen is used?

We began now by investigating, to what extent in an ordinary leucocyte-suspension i.e. without chloroform the phagocytosis depended on the oxygen-percentage of the medium.

For these investigations no carbon was used, because, as we know, this substance possesses the property of absorbing gases to a considerable extent. Instead of it we made use of amylum of rice-flour. The technical part had been worked out by Dr. J. DE HAAN, who, in consequence of the European war was prevented from completing his investigation. A detailed description of the technical part will, therefore, be published later on.

The principle for determining the degree of phagocytosis was the same as that for the taking up of carbon. It was namely determined which percentage of the leucocytes counted, had taken up amylum after a certain time.

I. *Comparison of the extent of the phagocytosis in a NaCl-solution which had been treated with nitrogen, with atmospheric air and with oxygen.*

As regards the way in which the experiments were carried out the following may be observed.

A thick suspension of horse-leucocytes in NaCl 0.9% is prepared in the manner we described before.<sup>2)</sup>

Further a considerable volume of NaCl-sol. 0.9% is boiled out, an increase in the concentration being obviated.

a. part is treated with nitrogen.

b. „ „ „ „ atmospheric air.

c. „ „ „ „ oxygen.

Thus NaCl-solutions with increasing oxygen-percentages were obtained. We satisfied ourselves of this by oxygen-determinations according to the method of WINKLER with manganous chloride, natrium-thiosulphate, hydrochloric acid and I in KI. 1 cubic centimetre of the thiosulphate-solution corresponds with 0.0782 mmg. of oxygen.

<sup>1)</sup> HEGER et BARUCH. Instit. Solvay 13 Fasc. 1; Bulletin de l'Acad. Royale de Médecine de Belgique Séance du 26 Juillet 1913.

<sup>2)</sup> Cf. inter alia. Physik. chem. Untersuchungen über Phagozyten. Wiesbaden, J. F. BERGMANN 1912.

A description of the method is given a.o. by HANS FILLIÉ, *Zeitschrift f. allgem. Physiol.* **8**, (1908) 496.

To 4 cc. of the solutions *a*, *b* and *c* 0,1 cc. of serum is added and to these mixtures 0.3 cc. of the thick leucocyte-suspension.

After they have been exposed to room-temperature for half an hour, during which time they were repeatedly stirred gently, 0.3 cc. of an amylum-suspension in NaCl 0.9 % is added to the suspensions, after which they are kept at 37° in an incubator. After 20 or 30 minutes they are simultaneously taken out and the phagocytosis is stopped by placing them in icewater and adding formol. Then preparations are made which are examined after.

The reader will have noticed that in these experiments serum is added. Unlike carbon, amylum is only taken up if the fluid contains some serum. The most desirable quantity amounts according to DE HAAN's researches to 2½ vol. percent. This was confirmed by OUWELEEN, who will soon publish further particulars in a dissertation.

Further particulars relating to the technicalities of the amylum-phagocytosis are omitted here. We can now proceed to summarize the results of one series of experiments in a table.

TABLE I.

Comparison of the extent of the phagocytosis in NaCl-solution, which had been treated with nitrogen, with oxygen and with atmospheric air. Phagocytes and amylum had been in contact for 20 minutes<sup>1)</sup>.

The leucocytes are in	Number of leucocytes counted	Number of leucocytes having taken up amylum	Percentage of leucocytes containing amylum
NaCl-solution <i>treated with nitrogen</i>	577	159	28.5 %
NaCl-solution <i>treated with air</i>	672	130	19.3 %
NaCl-solution <i>treated with oxygen</i>	835	110	13.1 %

<sup>1)</sup> If the leucocyte-suspension remains at 37° in contact with amylum for a longer time, the values denoting the extent of phagocytosis will be greater. But the differences in the degree of phagocytosis become smaller and smaller. At length a time will come when in all three fluids the phagocytosis is the same. This is the case mostly after about 1½ hour. The reason is that we have to do with a difference in velocity. Evidently the phagocytosis went slowest in the solution treated with oxygen, fastest in the one treated with nitrogen. If the phagocytes in the oxygen solution are left sufficient time, they will finally have taken up amylum in as ample a degree as the phagocytes in the nitrogen-medium in a shorter time.

This table brings the unexpected result, the phagocytosis is greatest where the slightest amount of oxygen was present.

We see namely that in the NaCl-solution treated with nitrogen the phagocytosis is about  $\frac{28-19}{19} \times 100 = 47\%$  greater than in the one treated with air; and in the latter again  $\frac{19-13}{13} \times 100 = 46\%$  greater than in the one treated with oxygen.

A repetition of the experiment when only the NaCl solutions were compared which had been treated with nitrogen and with oxygen gave a similar result.

TABLE II.  
Effect of nitrogen and of oxygen on phagocytosis.

In the fluid treated with <i>nitrogen</i>		22.2 %
" " " " " <i>oxygen</i>		17.6 "
" " " " " <i>nitrogen</i>		29.4 "
" " " " " <i>oxygen</i>		23.4 "

In the following series of experiments NaCl-solutions which had not been boiled out have been compared; some had been treated with nitrogen, others had not. This treatment consisted in N-gas (from a metal cylinder) being led for  $\frac{1}{2}$  hour into the bottle with NaCl-solution of 0.9% whilst the fluid was shaken every 5 minutes with the gas on the top of it.

It goes without saying that just as in the experiments of Tables I and II a complete expulsion of oxygen could not be expected, but this was not desired. If this had been aimed at, the suspension which was added afterwards, should also have been treated with N.

TABLE III.  
Effect of nitrogen on phagocytosis.

The fluid is not treated		It is treated with <i>nitrogen</i>
20.7 %		27.9 %
17.7 "		22.3 "
19.6 "		24 "
16.6 "		28.8 "

Here again the phagocytosis is increased everywhere by nitrogen. A new confirmation is supplied by the following series of experiments.

TABLE IV.  
Effect of a treatment with nitrogen on phagocytosis.  
Degree of phagocytosis.

The fluid is not treated	It is treated with nitrogen
22.9 %	26.1 %
23.8 "	33 "
23.2 "	27.8 "
20.5 "	31.2 "

Here again a higher degree of phagocytosis showed itself unmistakably, where only a slighter amount of oxygen was met with.

It must be noted that in two instances the results were different. It appeared namely that in one of the experiments the result was as follows :

in the NaCl-solution treated with *air* . . . . . phagocytosis 34.7%  
 " " " " " " *oxygen* . . . . . " 36 "

and in the other case :

NaCl-solution treated with *air* . . . . . phagocytosis 40.6%  
 " " " " " " *oxygen* . . . . . " 41.7 , ,

It is obvious, that an increased O-percentage has caused no decrease of the phagocytosis here, rather a slight increase. But these two results will have to be attributed either to mistakes in the experiment, or to individual differences, often met with in the phagocytes of different horses. The considerable amount of material which we have experimented with for many years, leaves no doubt about such differences. It has even occurred that the same horse which had been used 6 times at long intervals, and which had always supplied leucocytes that gave satisfactory results, gave cells the 7<sup>th</sup> time with which hardly any phagocytosis could be obtained.

This could not be attributed to the nature of the fluids, for with the same fluids another horse gave irreproachable results.

Yet in the results obtained with nitrogen, the possibility remained that this gas contained substances which had accelerated the phagocytosis. This was not very probable since the N, supplied by the

Company "Oxygenium" at Schiedam had been prepared by fractionated distillation of liquid air. It still contains about 1% of oxygen, further gases of the helium group, and a bit of oil-products due to the pumps. At any rate it seemed desirable to carry out experiments with hydrogen likewise.

## II. *Effect of hydrogen phagocytosis.*

These experiments were carried out like those with nitrogen. Here too compressed gas was used which had been purified in the usual way. The results, however, were different from what we had expected, the phagocytosis was found to have decreased instead of increased.

The phagocytosis was compared in fluids of which the NaCl-solution had not been treated, and which contained therefore comparatively much oxygen, with the phagocytosis in fluids of which the NaCl-solution had lost the greater part of its oxygen by being treated with H.

TABLE V.  
Effect of hydrogen on phagocytosis.  
Degree of phagocytosis.

The fluid is not treated	It is treated with hydrogen
24.5 %	14.7 %
20.9 "	14.9 "
18.9 "	20.7 "
21.9 "	18.1 "

The average of the first column comes to 21.5%, that of the second to 17.1%. There can be no doubt, therefore, but the hydrogen has impaired the phagocytosis.

The most obvious explanation was, that some noxious impurity had not been removed altogether. Therefore we used in the following experiments hydrogen which we had prepared ourselves from chemically pure zinc, which had been provided with a thin layer of copper by means of a copper-sulphate-solution of 5%.

Now the results were entirely different; *invariably the phagocytosis was promoted by the treatment with hydrogen.*

TABLE VI.  
Effect of Hydrogen on the phagocytosis  
Degree of Phagocytosis.

The fluid is not treated	It is treated with hydrogen
20.1 %	25.7 %
20.5 "	22.8 "
18.9 "	26.3 "
18.3 "	24.9 "

This table shows that if the salt-solution is not treated with hydrogen, the phagocytosis averages **19.4%**, if it is treated with hydrogen **24.9%**.

Besides these experiments several others were carried out, which *all resulted invariably in phagocytosis being promoted by the action of hydrogen.*

Only a few series of experiments must be more particularly drawn attention to. Their purpose was to investigate to what extent an intense hydrogen-treatment would produce another degree of phagocytosis than a less intense one.

It appeared then that a less intense treatment raised the phagocytosis from 41.2% to 47.1%, whilst an intense treatment only raised it to 45.4%.

It seemed to us that this must be due to the fact that an *extensive removal* of oxygen causes incipient paralysis, which will make itself the more felt as the oxygen is more completely removed.

If this view was correct, then it must be possible to lower the phagocytosis still more by a still more energetic removal of oxygen, nay to make it fall below that observed in the fluids not treated with hydrogen. It was indeed found possible to do so. We shall give an account of a few experiments taken with nitrogen.

### III. *Effect of an extensive removal of oxygen.*

A NaCl-solution of 0,9% is thoroughly treated with nitrogen; this is also done with the bloodserum, which we did not do as yet; of this serum 2½ vol. perc. is added to the NaCl-solution. Of this we take 4 ccm., add 0,3 ccm. of a thick leucocyte-suspension (in NaCl 0,9%) and leave the mixture exposed to roomtemperature for half an hour. Thus the leucocytes lose oxygen. Now 0,3 ccm. of a

suspension of amylum in NaCl-solution are added, which had likewise been treated with N, and the mixture thus obtained is exposed to the effect of body-temperature for 25 minutes.

If, however, the same experiment was carried out in exactly the same manner, but only with this difference that the fluid treated with nitrogen could act at room-temperature *for 5 hours instead of half an hour* on the phagocytes, then the phagocytosis was found to be much less than in the original fluid, which had not been treated with nitrogen. Hence after a longer exposure of the phagocytes to a medium which contains little oxygen, paralysis will set in, the available amount of oxygen being consumed to a great extent.

This may appear from the following experiments.

TABLE VII.

Effect of an extensive withdrawal of O on phagocytosis by a long exposure of the phagocytes to the normal medium and to the medium treated with N.

	Phagocytosis
After a 5 hours' exposure of the phagocytes to the serous NaCl-sol. which had <i>not</i> been treated with N.	$\frac{681}{1341} \times 100 = 50.71\%$
After a 5 hours' exposure of the phagocytes to the serous NaCl-sol. which <i>had</i> been treated with N.	$\frac{521}{1174} \times 100 = 44.38\%$

Whilst formerly after an exposure of one hour an increased phagocytosis was invariably observed, this increase has changed into a decrease after a 5 hours' exposure.

We shall add another experiment, showing the effect on the *same* leucocytes of an exposure of  $\frac{1}{2}$  hour and  $4\frac{1}{2}$  hours.

TABLE VIII.

Effect of a short and of a long exposure of the phagocytes to a solution containing only traces of oxygen.

Exposure of $\frac{1}{2}$ hour	Exposure of $4\frac{1}{2}$ hours
In the normal serous NaCl-sol.: $\frac{244}{941} \times 100 = 25.9\%$	In the normal serous NaCl-sol.: $\frac{443}{1125} \times 100 = 39.4\%$
In the serous NaCl-sol. contain. a trace of O: $\frac{321}{930} \times 100 = 34.5\%$	In the serous NaCl-sol. contain. a trace of O: $\frac{372}{1145} \times 100 = 32.5\%$

Hence we see that the same phagocytes which, after being exposed to nitrogen for half an hour, give a considerable increase viz.

$$\frac{34.5 - 25.9}{25.9} \times 100 = 33.2\%$$

show a *decreased* phagocytosis of

$$\frac{39.4 - 32.5}{39.4} \times 100 = 17.5\%$$

after an action of  $4\frac{1}{2}$  hours, the loss of O having become greater in that time. A longer exposure to the medium containing little O would probably have lowered the phagocytosis still more. The phagocytes will consume more and more their own oxygen.

IV. *Respiratory centre and phagocytosis. Effect of carbonic acid and of potassium cyanide. Discussion of the results obtained.*

If we submit the results obtained to a close examination, we are struck by the agreement between the effect which a withdrawal of oxygen has on the respiratory centre on the one hand, and on the phagocytes on the other.

After the many researches on the respiratory centre we may take it for granted that, besides by the action of carbonic acid, the respiratory centre is also stimulated by a withdrawal of oxygen.

If in an animal the O-percentage of the blood is increased by frequent deep respiration, then this respiration may be stopped for some time without the animal showing any need of it (apnoea). Under these circumstances the stimulus passing from the respiratory centre on to the nerve centres of the respiratory muscles is evidently too weak to act upon it successfully. Likewise with the phagocytes we observe that a considerable increase of the O-supply leads to a decreased activity, a decreased phagocytosis. *If the O-percentage decreases, the phagocytes are stimulated into a higher activity, the phagocytosis increases, while it decreases more and more, subsequently, as more O is lost, in accordance with the fact that all cells of the animal organism need oxygen, if they are to continue their functions.*

The respiratory centre too increases its activity when O is very scarce (dyspnoea), and is paralyzed when O continues to be withdrawn.

Hitherto we have made no quantitative comparisons between the O-percentage of the fluid in which the phagocytes are paralyzed, and that in which the nervous centre refuses to act. These comparisons, however, can only relate to the medium, hardly to the cells themselves. In view of these considerations and also owing to the fact that a quantitative determination of phagocytosis is very tiresome, no experiments have been made in this direction. It may be expected that the respiratory centre will be more sensitive to a withdrawal of oxygen than the phagocytes. The higher nervous centres are certainly still more sensitive than the respiratory centre.

In view of this agreement between phagocytes and respiratory centre the question suggests itself whether other substances have likewise the same effect on both.

Therefore we have in the first place investigated the effect of *carbonic acid* on phagocytosis. Some years ago already we published investigations on the effect of  $\text{CO}_2$  on phagocytes, and arrived at the conclusion that the use of somewhat large amounts of  $\text{CO}_2$  had an injurious effect on phagocytosis<sup>1)</sup>. The effect of slight quantities was not investigated then.

Now that we had a more accurate method at our disposal, it became desirable to repeat the experiments with slighter quantities of  $\text{CO}_2$ .

NaCl-solutions were made with different  $\text{CO}_2$ -percentages by mixing different quantities of a boiled out NaCl-solution with the same NaCl-solution which had been saturated with  $\text{CO}_2$ .

We prepared the following mixtures: containing

4 Vol. NaCl-sol.	+ 1 Vol. of the NaCl-sol. saturated with $\text{CO}_2$ .	35 Vol. pct $\text{CO}_2$
9 " "	+ 1 Vol. " " " " " "	17.5 " " "
19 " "	+ 1 Vol. " " " " " "	8.75 " " "
49 " "	+ 1 Vol. " " " " " "	3.5 " " "
99 " "	+ 1 Vol. " " " " " "	1.75 " " "

TABLE IX.  
Effect of  $\text{CO}_2$  on phagocytosis.

Boiled out NaCl-sol. containing:	Phagocytosis
no $\text{CO}_2$	46.3 %
35 Vol. Perc. $\text{CO}_2$	0
17.5 " " "	0.7 %
8.75 " " "	4.2 "
3.5 " " "	41.9 "
1.75 " " "	42 "

This table shows that carbonic acid has effected an entire or entire paralysis of the phagocytosis, except in the concentrations 3.5 % and 1.75 %.

<sup>1)</sup> HAMBURGER. VIRSCHOW'S Archiv 156 (1899), 329.

Now the question was whether perhaps below, or in the neighbourhood of the concentration of 1.75 %, there would not be one, in which the phagocytosis was increased. Therefore the experiment was repeated also with weaker concentrations.

TABLE X.  
Effect of CO<sub>2</sub> on phagocytosis.

Boiled out NaCl-sol. containing	Phagocytosis
no CO <sub>2</sub>	$\frac{145}{519} \times 100 = 27.9\%$
17.5 Vol. percent CO <sub>2</sub>	0
3.5 " " "	$\frac{150}{565} \times 100 = 26.7\%$
1.75 " " "	$\frac{159}{497} \times 100 = 31.9\%$
0.35 " " "	$\frac{148}{492} \times 100 = 30\%$
0.175 " " "	$\frac{140}{506} \times 100 = 27.6\%$

From this series of experiments it appears, just as from the preceding table, that in the NaCl-solution containing 17.5 % CO<sub>2</sub> the phagocytosis is 0, in that containing 3.5 % about the same as if there had been no CO<sub>2</sub> in it. At 1.75 vol. perc. *the phagocytosis has risen 14.2 %* and at 0.35 vol. perc. CO<sub>2</sub>, 7 %. At 3.5 vol. perc. the promotive action is therefore compensated by the noxious effect peculiar to CO<sub>2</sub>.

*Consequently this series of experiments plainly demonstrates that in weak concentrations carbonic acid increases the phagocytosis, and that in higher concentrations it has a paralyzing effect.*

We shall adduce no more experiments in this short article. Let the statement suffice that the result was repeatedly and invariably confirmed.

It should, however, be pointed out that the amount of CO<sub>2</sub>, required to effect an increase (or also a paralysis) will have to be greater when the phagocytes are surrounded by serum, than in our experiments where the medium was a NaCl-solution containing only 2½ vol. perc. of serum. On another occasion we shall, for a different

purpose, (the effect of artificial venous congestion on the phagocytosis of bacteria) determine the amount of  $\text{CO}_2$  which accelerates phagocytosis when only serum is used.

*At any rate it may now be looked upon as an established fact that, as regards carbonic acid, the phagocytes behave exactly like the respiratory centre.* For the respiratory centre is also stimulated by slight quantities and paralyzed by greater ones.

As we know, *potassiumcyanide* has a highly stimulating effect on the respiratory centre before paralysis sets in. A violent dyspnoea manifests itself.

It is all but certain that this symptom must be connected with the property this substance has of obstructing the oxygen-consumption of the cells. This becomes manifest, for instance, when we note the effect of KCN on muscular contraction. Even if to the blood with which the muscle is supplied, oxygen is added in an ample degree, traces of potassiumcyanide lower the oxygen-consumption considerably.

What may be the effect of potassiumcyanide on phagocytosis?  
The following tables will supply an answer.

TABLE XI.

Effect of KCN on phagocytosis.

Serous NaCl-solution + KCN	Phagocytosis
0	12.1 %
1 : 1000	0
1 : 2000	0
1 : 5000	6.6 %
1 : 10.000	9.7 „
1 : 50.000	23.9 „
1 : 100.000	19.2 „

From this table it appears that in a concentration of 1 to 1000 and also of 1 : 10000, KCN has had a noxious, but on the other hand in weaker concentrations, a favourable effect on phagocytosis.

The following table contains experiments also with weaker concentrations.

TABLE XII.  
Effect of KCN on phagocytosis.

Serous NaCl-sol. + KCN	Phagocytosis
0	$\frac{187}{622} \times 100 = 30 \%$
1 : 10.000	$\frac{204}{564} \times 100 = 36.1 \%$
1 : 50.000	$\frac{289}{675} \times 100 = 42.8 \%$
1 : 100.000	$\frac{231}{624} \times 100 = 36.8 \%$
1 : 1000.000	$\frac{185}{617} \times 100 = 29.9 \%$

Hence we see that in slight quantities potassiumcyanide has a highly stimulating effect on phagocytosis, which is checked by greater quantities. Here again a perfect agreement in the behaviour of respiratory centre and phagocytes.

V. *Explanation of the stimulating effect of traces of chloroform on phagocytosis, and of the excitement-stage in narcosis.*

Let us now return to our startingpoint, viz. to the question what may be the reason why traces of chloroform and similar substances cause an acceleration of phagocytosis.

By VERWORN and his school it has been demonstrated that in the chloroform-narcosis the cells have lost the power of using the oxygen offered to them, for oxydation purposes. There is asphyxia. The supposition suggests itself that *the application of small amounts of chloroform brings about this blockade of oxygen imperfectly, and that the phagocytes are thus reduced to a condition similar to that which is met with when a short treatment with nitrogen and hydrogen has caused them to lose part of their oxygen, which loss has brought them into a state of increased sensitiveness.*

The action of greater amounts of chloroform will cause the potential oxygen percentage, if we may call it thus, to fall still lower, the phagocytosis will begin to decrease: a decrease which likewise sets in at a long action of a medium containing little oxygen, as we obtained it by treatment with nitrogen or hydrogen. (Comp. § III).

We have tested this view experimentally, for instance by allowing

chloroform and nitrogen to act together under various conditions as regards time and concentration. But we shall omit giving an account of these experiments to restrict the size of this paper. Moreover a detailed report will, as we said before, be published elsewhere.

*And now the excitement-stage in narcosis.*

If we let the various narcosis-theories pass in review, then it appears that not a single one *has even attempted* to give an explanation of the excitement-stage. Our researches on phagocytosis, and the agreement in the conduct of respiratory centre and phagocytes enable us to do so.

When MAX VERWORN in his article "Narkose" in the "Handbuch der Naturwissenschaften" B. VII, 1912, has explained that, in his opinion, narcosis is nothing but a consequence of *acute asphyxia*, and adds a few words on the attendant symptoms in narcosis, he expresses himself as follows:

"Es ist nicht wahrscheinlich, dass diese Nebenwirkung (Excitationsstadium) ebenfalls aus dem einem Punkte der Oxydationslähmung in der Zelle entspringt, *doch fehlt für die Genese dieser Nebenwirkung bisher noch jede Analyse*".

Our investigations of the origin of an increased phagocytosis by oxygen-withdrawal, have shown that also the excitement-stage in narcosis is in perfect agreement with the fact stated by VERWORN in his narcosis theory.

*We need only conceive that at the beginning of the narcosis, owing to a decrease in the amount of available oxygen, the sensibility of the higher nervecentres is heightened.*

If the chloroform-inhalation is continued, this sensibility will decrease, owing to a further decrease of the potential O-percentage, and finally narcosis will set in. Whether the state of complete narcosis is partly due to other factors, for instance to a semi-coagulation of the protoplasm in the sense of CLAUDE BERNARD, or to a decrease of dispersity of enzymes etc. need not be considered here. First the higher centres which are, as we know, very sensitive to oxygen withdrawal, are paralyzed, then the spinal centres and after that the respiratory centre.

We may add that in the first stage of narcosis not only the higher cortical centres and the spinal centres pass through an excitement-stage, but according to researches of KNOLL and of ARLOING the respiratory centre is also in a state of heightened irritability.

The question which first suggests itself, is the following: how is it that a decrease of the available oxygen-percentage heightens the irritability of the phagocytes (and ganglion cells).

We might suppose that — as regards the phagocytes — the withdrawal of oxygen affects in the first place the surface of the cells; owing to this fact the surface layer will plunge into their inner part which contains more oxygen; thus the amoeboid motion would be accentuated. The phenomenon would remind of the chemotactical motion of bacteria to an airbubble. In the case of phagocytes we might speak of an “entochemotaxis”, if I may be allowed to call it so.

But it might also be assumed that a withdrawal of oxygen causes a decreased viscosity in the cells.

[I have indeed found that if yolk is treated with oxygen, the viscosity increases, whence it follows that the viscosity is indeed affected by the oxygen percentage. Albuminous solutions were not so affected; we must, therefore, think of lipid substances, and in this we are strengthened by observations of THUNBERG, which were amply confirmed by WARBURG, viz. that lecithin in the presence of iron can bind oxygen in relatively great quantities. They think that an oxydative decomposition of lecithin takes place, but could find no oxydation-products. In my opinion we have to deal here with a compound of lecithin iron, which, like haemoglobin, can bind oxygen in a dissociable form.

In this way oxygen might be supplied in a concentrated form to the oxydable substances in the cell. It is the task of the red blood-corpuscles to supply on their way through the capillaries, and by means of plasma and lymph, the oxygen required for the tissue-cells].<sup>1)</sup>

In this direction my investigations are continued. More problems suggest themselves which will not be discussed now.

#### S U M M A R Y.

1. *If phagocytes are exposed during half an hour to a medium from which O has been almost entirely removed, they display a considerable acceleration of phagocytosis.*

If the cells are left for a longer time, e. g. 5 hours, in this solution, then the acceleration of the phagocytosis will give way to a retardation.

2. For this *acceleration of the phagocytosis* by lack of O, which may seem strange at a first glance, and which was indeed unexpected, an *analogy may be found in the respiratory centre*. Here too lack of O heightens the irritability (dyspnoea), the respiration ceasing entirely when the amount of O is further decreased.

3. This view is confirmed *by the corresponding behaviour of both cellspecies when exposed to KCN.*

<sup>1)</sup> [ ] Note added to the translation.

It is well-known that this substance checks the O-consumption. When applied in traces, which renders the check imperfect, KCN was found to accelerate phagocytosis considerably. On the respiratory centre the effect of slight quantities of KCN is the same: Violent respiratory movements set in. Greater quantities cause paralysis in both cases.

4. *Also as regards carbonic acid an analogy is found between phagocytes and respiratory centre.* Traces of  $\text{CO}_2$  were discovered to promote phagocytosis, whilst greater quantities decreased it. As we know the irritability of the respiratory centre is likewise increased by  $\text{CO}_2$ , but the centre is paralyzed by an excess of  $\text{CO}_2$  in the blood.

5. The facts and views set forth here, supply an obvious answer to the question which formed the starting-point of the present investigation: *why do traces of chloroform and other fat-dissolving substances cause an acceleration of phagocytosis?*

The numerous researches of VERWORN and his pupils on narcosis have established the fact that narcotics such as chloroform have the property of impeding the O-consumption by the cells (spinal centres, nerve-fibres, amoebae etc.). Now it is obvious that as long as mere traces of chloroform are acting, only part of the available oxygen will be rendered useless, in other terms, the blockade of the oxygen will be incomplete. And then the phagocytes are in the case of the experiments mentioned sub 1, where partial removal of oxygen by nitrogen or hydrogen causes an acceleration of the phagocytosis. This acceleration gradually passes into a retardation in proportion as the store of oxygen of the cell becomes more exhausted; an exhaustion which sets in quickly when, for instance by the administration of larger amounts of chloroform, the oxygen-consumption has fallen to a minimum or has ceased altogether.

b. The explanation given sub 5 of the acceleration of phagocytosis by traces of chloroform is in perfect agreement with the fact that *in the first stage of chloroform-narcosis the irritability of the respiratory-centre is increased. Likewise the excitement-stage is explained, which manifests itself at the beginning of the narcosis, and which hitherto none of the narcosis theories have so much as attempted to explain.* (Cf. note 3 p. 1326).

Here too, with the higher nerve-centres, the explanation must be sought in a heightened sensitiveness in consequence of an incipient

lack of oxygen, which increases if the chloroform inhalation is continued, and finally leads to a paralysis of consciousness. When this sets in, the respiratory centre has not been paralyzed yet. It is indeed a well-known fact that the higher brain-centres are more sensitive to oxygen-withdrawal than all other cells of the body.

Probably the increased sensitiveness, as a result of a partial oxygen-withdrawal, must be looked upon as a general phenomenon. The sensitiveness of the vomit-centre for instance decreases, just like that of respiratory centre and phagocytes, if more oxygen is supplied. Hence the inclination to vomit may be subdued to some extent by frequent and deep breathing, whilst it is stimulated by lack of oxygen.

*Groningen, March 1915.*

*Physiological Laboratory.*

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**(June 3, 1915).**

# CONTENTS.

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- ABEL's polynomials (On HERMITE's and). 192.
- ABSORPTION LINES  $D_1$  and  $D_2$  (On the structure of the). 720.
- AIR-BLADDER (The physiology of the) of fishes. 1088.
- ALBUMINOUS FLUIDS (The identification of traces of bilirubin in). 807.
- ALKALIES (The coloration of some derivatives of Picrylmethylamide with). 647.
- ALLOTROPY (The) of cadmium. II. 54. III. 122. IV. 638. V. 1050.
- of zinc. II. 59. III. 641.
  - of copper. II. 60.
  - of antimony. I. 645.
  - of lead. I. 822. Note. 1055.
  - of potassium. I. 1115.
  - of bismuth. II. 1236.
  - (The application of the theory of) to electromotive equilibria. II. 37. III. 680.
  - (The metastability of metals in consequence of) and its significance for Chemistry, Physics and Technics. 200. III. 926. IV. 1238.
  - (The metastable continuation of the mixed crystal series of pseudo-components in connection of the phenomenon). II. 672.
- ALMOND (Gummosis in the fruit of the) and the Peachalmond as a process of normal life. 810.
- AMIDES of  $\alpha$ -oxyacids (Action of sodium-hypochlorite on). 1163.
- AMMONIA (On the interaction of) and methylamine on 2,3,4-trinitrodimethylaniline. 1034.
- AMMONIA-water (The system). 182.
- AMORPHOUS CARBON (The decoloration of fuchsin-solutions by). 1322.
- Anatomy.** P. RETHIG and C. U. ARIËNS KAPPERS: "Further contributions to our knowledge of the brain of *Myxine glutinosa*". 2.
- C. WINKLER: "A case of occlusion of the arteria cerebelli posterior inferior". 914.
  - J. BOEKE: "On the termination of the efferent nerves in plain muscle-cells, and its bearing on the sympathetic (accessory) innervation of the striated muscle-fibre". 982.
  - J. BOEKE: "On the mode of attachment of the muscular fibre to its tendonfibres in the striated muscles of the vertebrates". 989.
  - H. A. VERMEULEN: "The vagus area in Camelidae". 1119.
- ANOMALIES (On SEELIGER's hypothesis about the) in the motion of the inner planets. 23.
- ANTIBODIES (On the formation of) after injection of sensitized antigens. II. 318.

- ANTIGENS (On the formation of antibodies after injection of sensitized). II. 318.
- ANTIMONY (The allotropy of). I. 645.
- APOPHYLLITE (On the real symmetry of cordierite and). 430.
- ARIËNS KAPPERS (C. U.), v. KAPPERS (C. U. ARIËNS).
- ARSENIC TRISULPHIDE SOLS (The connection between the limit value and the concentration of). 1158.
- ARSENIUS OXIDE (Compounds of). I. 1111.
- ARTERIA cerebelli posterior inferior (A case of occlusion of the). 914.
- Astronomy.** J. WOLTJER JR.: "On SEELIGER's hypothesis about the anomalies in the motion of the inner planets". 23.
- W. DE SITTER: "Remarks on Mr. WOLTJER's paper concerning SEELIGER's hypothesis". 33.
- W. DE SITTER: "The figure of the planet Jupiter". 1047.
- W. DE SITTER: "On the mean radius of the earth, the intensity of gravity and the moon's parallax". 1291.
- W. DE SITTER: "On isostasy, the moments of inertia and the compression of the earth". 1295.
- W. DE SITTER: "The motions of the lunar perigee and node and the figure of the moon". 1309.
- A'TEN (A. H. W.) and A. SMITS. The application of the theory of allotropy to electro-motive equilibria. II. 37. III. 680.
- ATLANTIC OCEAN (On the relation between departures from the normal in the strength of the trade-winds of the) and those in the waterlevel and temperature in the Northern European seas. 1147.
- ATOMIC FORCES (The calculation of the molecular dimensions from the supposition of the electric nature of the quasi-elastic). 877.
- B A A T (W. C. D E) and F. A. H. SCHREINEMAKERS. The system: copper sulphate, copper chlorid, potassium sulphate, potassium chlorid and water at 30° C. 533.
- On the quaternary system  $KCl-CuCl_2-BaCl_2-H_2O$ . 781.
- Compounds of the arsenious oxide. I. 1111.
- B A C K E R (H. J.) and A. P. N. FRANCHIMONT. The coloration of some derivatives of picrylmethylamide with alkalies. 647.
- $\alpha$ -Sulpho-propionic acid and its resolution into optically active isomerides. 653.
- B A K H U Y Z E N (H. G. V A N D E S A N D E). Comparison of the Dutch platinum-iridium Metre N<sup>o</sup>. 27 with the international Metre *M* as derived from the measurements by the Dutch Metre Commission in 1879 and 1880, and a preliminary determination of the length of the measuring-bar of the French base apparatus in international metres. 311.
- N. WILDEBOER and J. W. DIEPERINK: "Comparison of the measuring bar used in the base measurement at Stroe with the Dutch Metre N<sup>o</sup>. 27. 300.
- BASE MEASUREMENT (Comparison of the measuring bar used in the) at Stroe with the Dutch Metre No. 27. 300.
- B E E G E R (N. G. W. H.). On HERMITE's and ABEL's polynomia. 192.
- BENZENE DERIVATIVES (The replacement of substituents in). 1027.

- BENZENES (The nitration of the mixed dihalogen). 846.
- BEIJERINCK (M. W.). Gummosis in the fruit of the Almond and the Peachalmond as a process of normal life. 810.
- BILIRUBIN (The identification of traces of) in albuminous fluids. 807.
- BINARY MIXTURES (Isothermals of monatomic substances and their). XVI. 275.  
— (Isothermals of di-atomic substances and their). XV. 950. XVI. 959.
- BINARY SYSTEM (On unmixing in a) for which the three-phase pressure is greater than the sum of the vapour tensions of the two components. 834.
- BISMUTH (The allotropy of). II. 1236.
- BOEKE (J.). On the termination of the efferent nerves in plain muscle-cells and its bearing on the sympathetic (accessory) innervation of the striated muscle-fibre. 982.  
— On the mode of attachment of the muscular fibre to its tendonfibres in the striated muscles of the vertebrates. 939.  
— presents a paper of Dr. A. B. DROOGLEEVER FORTUYN: "The decoloration of fuchsin-solutions by amorphous carbon". 1322.
- BOER (S. DE). On the heart-rhythm. 1075 II. 1135.
- BÖESEKEN (J.). On catalyse. 546.  
— and W. D. COHEN. The reduction of aromatic ketones. III. Contribution to the knowledge of the photochemical phenomena. 849.
- BOILING POINTS (The influence of the hydration and of the deviations from the ideal gas-laws in aqueous solutions of salts on the solidifying and the). 1036.
- BOIS (H. DU). Modern electromagnets, especially for surgical and metallurgic practice. 468.  
— The universality of the ZEEMAN-effect with respect to the STARK-effect in canal-rays. 873.
- BOKHORST (S. C.) and A. SMITS. On the vapour pressure lines in the system phosphorus. II. 678. III. 962.  
— Further particulars concerning the system phosphorus. 973.
- BOLK (L.) presents a paper of Dr. P. RÖTHIG and Dr. C. U. ARIËNS KAPPERS: "Further contributions to our knowledge of the brain of *Myxine glutinosa*". 2.  
— presents a paper of Dr. H. A. VERMEULEN: "The vagus area in *Camelidae*". 1119.
- BOSCH (J. C. VAN DEN) and ERNST COHEN. The allotropy of antimony. I. 645.
- Botany.** Miss LUCIE C. DOYER: "Energy transformations during the germination of wheat-grains". 62.  
— M. W. BEIJERINCK: "Gummosis in the fruit of the Almond and the Peachalmond as a process of normal life". 810.  
— C. E. B. BREMEKAMP: "The mutual influence of phototropic and geotropic reactions in plants". 1278.
- BRAIN of *Myxine glutinosa* (Further contributions to our knowledge of the). 2.
- BRAVAIS (The theory of) (on errors in space) for polydimensional space with applications to correlation (Continuation). 150.
- BREMEKAMP (C. E. B.). On the mutual influence of phototropic and geotropic reactions in plants. 1278.

- BROUWER (H. A.). On the granitic area of Rokan (Middle-Sumatra) and on contact phenomena in the surrounding schists. 1190.
- BRUIN (G. D E). A crystallized compound of isoprene with sulphur dioxide. 585.  
— and ERNST COHEN. The metastability of the metals in consequence of allotropy, and its significance for Chemistry, Physics and Technics. III. 926.
- BÜCHNER (E. H.) and L. K. WOLFF. On the behaviour of gels towards liquids and the vapours thereof. II. 92.
- CADMIUM (The allotropy of). II. 54. III. 122. IV. 638. V. 1050.
- CAMELIDAE (The vague area in). 1119.
- CANAL-RAYS (The universality of the ZEEMAN-effect with respect to the STARK-effect in). 873.
- CAPILLARY PRESSURE (On the measurement of the) in a soap-bubble. 946.
- CAPILLARITY (Measurements on the) of liquid hydrogen. 528.
- CATALYSE (On). 546.
- CHEMICAL CONSTANT (The) and the application of the quantumtheory by the method of the natural vibrations to the equation of state of an ideal monatomic gas. 20.
- Chemistry.** A. SMITS and A. H. W. ATEN: "The application of the theory of allotropy to electromotive equilibria". II. 37. III. 680.  
— E. COHEN and W. D. HELDERMAN: "The allotropy of cadmium. II. 54. III. 122. IV. 638. V. 1050.  
— E. COHEN and W. D. HELDERMAN: "The allotropy of zinc." II. 59. III. 641.  
— E. COHEN and W. D. HELDERMAN: "The allotropy of copper". II. 60.  
— F. A. H. SCHREINEMAKERS: "Equilibria in ternary systems". XV. 70. XVI. 169. XVII. 767. XVIII. 1260.  
— L. K. WOLFF and E. H. BÜCHNER: "On the behaviour of gels towards liquids, and the vapours thereof". II. 92.  
— A. SMITS and S. POSTMA: "The system ammonia-water". 182.  
— ERNST COHEN: "The metastability of the metals in consequence of allotropy and its significance for Chemistry, Physics and Technics". 200.  
— F. M. JAEGER and ANT. SIMEK: "Studies in the field of Silicate-chemistry". II. 239. III. 251.  
— F. M. JAEGER: "The temperature-coefficients of the free surface-energy of liquids at temperatures from  $-80^{\circ}$  to  $1650^{\circ}$  C. I. 329. F. M. JAEGER and M. SMIT. II. 365. III. 386. F. M. JAEGER and J. KAHN. IV. 395. F. M. JAEGER. V. 405. VI. 416. VII. 555. VIII. 571.  
— F. A. H. SCHREINEMAKERS and Miss W. C. DE BAAT: "The system: copper sulphate, copper chlorid, potassium sulphate, potassium chlorid and water at  $30^{\circ}$  C." 533.  
— J. BÖESEKEN: "On catalyse". 546.  
— G. DE BRUIN: "A crystallized compound of isoprene with sulphur dioxide". 585.  
— H. R. KRUYT: "Current potentials of electrolyte solutions". 615.  
— H. R. KRUYT: "Electric charge and limit value of colloids". 623.  
— ERNST COHEN and J. C. VAN DEN BOSCH: "The allotropy of antimony". I. 645.

- Chemistry.** A. P. N. FRANCHIMONT and H. J. BACKER: "The coloration of some derivatives of Picrylmethylamide with alkalis". 647.
- A. P. N. FRANCHIMONT and H. J. BACKER: " $\alpha$  Sulpho-propionic acid and its resolution into optically active isomerides". 653.
- A. SMITS: "The metastable continuation of the mixed crystal series of pseudo-components in connection with the phenomenon allotropy". II. 672.
- A. SMITS and S. C. BOKHORST: "On the vapour pressure lines of the system phosphorus". II. 678.
- F. E. C. SCHEFFER: "On gas equilibria and a test of Prof. v. D. WAALS JR.'S formula". I. 695. II. 1011.
- W. REINDERS: "Equilibria in the system Pb-S-O, the roasting reaction process". 703.
- F. A. H. SCHREINEMAKERS and Miss W. C. DE BAAT: "On the quaternary system  $KCl-CuCl_2-BaCl_2-H_2O$ ". 781
- ERNST COHEN and W. D. HELDERMAN: "The allotropy of lead". 822. Note. 1055.
- A. F. HOLLEMAN: "The nitration of the mixed dihalogenbenzenes". 846.
- J. BÖESEKEN and W. D. COHEN: "The reduction of aromatic ketones. III. Contribution to the knowledge of the photo-chemical phenomena". 849.
- ERNST COHEN and G. DE BRUIN: "The metastability of the metals in consequence of allotropy and its significance for Chemistry, Physics and Technics". III. 926.
- A. SMITS and S. C. BOKHORST: "On the vapour pressure lines of the system phosphorus". II. 678. III. 962.
- A. SMITS and S. C. BOKHORST: "Further particulars concerning the system phosphorus". 973.
- A. F. HOLLEMAN: "The replacement of substituents in benzene derivatives". 1027.
- P. VAN ROMBURGH and Miss D. W. WENSINK: "On the interaction of ammonia and methylamine on 2,3,4-trinitrodimethylaniline". 1034.
- C. H. SLUITER: "The influence of the hydration and of the deviations from the ideal gas-laws in aqueous solutions of salts on the solidifying and the boiling points". 1036.
- Miss ADA PRINS: "On critical end-points and the system ethanenaphtalene". 1095.
- F. A. H. SCHREINEMAKERS and Miss W. C. DE BAAT: "Compounds of the arsenious oxyde". 1111.
- ERNST COHEN and S. WOLFF: "The allotropy of potassium". I. 1115.
- H. R. KRUYT and JAC. VAN DER SPEK: "The connection between the limit value and the concentration of arsenic trisulphide sols". 1158.
- R. A. WEERMAN: "Action of sodium hypochlorite on amides of  $\alpha$ -oxyacids". 1163.
- F. M. JAEGER: "Researches on PASTEUR'S principle of the connection between molecular and physical dissymmetry". I. 1217.
- ERNST COHEN: "The allotropy of bismuth". II. 1236.
- ERNST COHEN and W. D. HELDERMAN: "The metastability of the metals in consequence of allotropy and its significance for Chemistry, Physics and Technics". IV. 1238.

- Chemistry.** A. W. K. DE JONG: "Action of sunlight on the cinnamic acids". 1274.
- CINNAMIC ACIDS (Action of sunlight on the). 1274.
- CIRCLES (Systems of) determined by a pencil of conics. 1107.
- COHEN (ERNST). The metastability of the metals in consequence of allotropy, and its significance for Chemistry, Physics and Technics. II. 200.
- presents a paper of DR. H. R. KRUYT: "Current potentials of electrolyte solutions". 615.
  - presents a paper of Dr. H. R. KRUYT: "Electric charge and limit value of colloids". 623.
  - presents a paper of Dr. H. R. KRUYT and JAC. VAN DER SPEK: "The connection between the limit value and the concentration of arsenic trisulphide sols". 1158.
  - The allotropy of bismuth. II. 1236.
  - and J. C. VAN DEN BOSCH. The allotropy of antimony. I. 645.
  - and G. DE BRUIN. The metastability of the metals in consequence of allotropy and its significance for Chemistry, Physics and Technics. III. 926.
  - and W. D. HELDERMAN. The allotropy of Cadmium. II. 54. III. 122. IV. 638. V. 1050.
  - The allotropy of zinc. II. 59. III. 541.
  - The allotropy of copper. II. 60.
  - The allotropy of lead. I. 822. Note 1055.
  - The metastability of the metals in consequence of allotropy and its significance for Chemistry, Physics and Technics. IV. 1238.
  - and S. WOLFF. The allotropy of potassium. I. 1115.
- COHEN (W. D.) and J. BÖSEKEN. The reduction of aromatic ketones. III. Contribution to the knowledge of the photochemical phenomena. 849.
- COLLOIDS (Electric charge and limit value of). 623.
- COLORATION (The) of some derivatives of Picrylmethylamide with alkalies. 647.
- COLOURS (On FRESNEL's coefficient for light of different). 1<sup>st</sup> part. 415.
- COMPOUND (A crystallized) of isoprene with sulphur dioxide. 585.
- COMPOUNDS of arsenious oxide. I. 1111.
- CONCENTRATION (The connection between the limit value and the) of arsenic trisulphide sols. 1158.
- CONGRUENCE (A bilinear) of rational twisted quintics. 1250.
- CONGRUENCES (Some particular bilinear) of twisted cubics. 1256.
- CONICS (Systems of circles determined by a pencil of). 1107.
- CONTACT-PHENOMENA (On the granitic area of Rokan (Middle-Sumatra) and on) in the surrounding schists. 1190.
- COPPER (The allotropy of). II. 60.
- (Measurements on the specific heat of lead between 14° and 80° K. and of between 15° and 22° K. 894.
- COPPER SULPHATE, Copper chlorid (The system :), potassium sulphate, potassium chlorid and water at 30°. 533.
- CORDIERITE and Apophyllite (On the real symmetry of). 430.

- CORRELATION** (The theory of BRAVAIS (on errors in space) for polydimensional space, with applications to) (Continuation), 150.
- CORRESPONDING STATES** (Contribution to the theory of), 840.
- CRITICAL POINT** (Vapour pressures of oxygen and) of oxygen and nitrogen, 950.
- CRITICAL QUANTITIES** (A new relation between the) and on the unity of all substances in their thermic behaviour, 451.
- (Some remarks on the values of the) in case of association, 598.
- CROMMELIN** (C. A.). Isothermals of monatomic substances and their binary mixtures, XVI, 275.
- Isothermals of di-atomic substances and their binary mixtures, XVI, Vapour pressures of nitrogen between the critical point and the boiling point, 959.
- E. MATHIAS and H. KAMERLINGH ONNES. The rectilinear diameter of nitrogen, 953.
- CRYSTAL SERIES** (The metastable continuation of the mixed) of pseudo-components in connection with the phenomenon allotropy, II, 672.
- CRYSTALS** (On a new phenomenon accompanying the diffraction of RÖNTGEN rays in birefringent), 1204.
- CUBE** (The different ways of floating of an homogeneous), 224.
- CUBICS** (Some particular bilinear congruences of twisted), 1256.
- CURVES** (Characteristic numbers for nets of algebraic), 935.
- (Characteristic numbers for a triply infinite system of algebraic plane), 1055.
- DECOLORATION** (The) of fuchsin-solutions by amorphous carbon, 1322.
- DEEP reflexes** (Exaggeration of), 885.
- DENSITY** (On the manner in which the susceptibility of paramagnetic substances depends on the), 110.
- (Accidental deviations of) and opalescence at the critical point of a single substance, 793.
- DIAMETER** (The rectilinear) of nitrogen, 953.
- DIEPERINK** (J. G.), N. WILDEBOER and H. G. VAN DE SANDE BAKHUYZEN. Comparison of the measuring bar used in the base measurement at Stroe with the Dutch Metre N<sup>o</sup>. 27, 300.
- DIFFRACTION** (On a new phenomenon accompanying the) of Röntgen rays in birefringent crystals, 1204.
- DIFFUSION COEFFICIENT** (The) of gases and the viscosity of gas-mixtures, 1068.
- DISCONTINUITIES** (On apparent thermodynamic) in connection with the value of the quantity  $b$  for infinitely large volume, 606.
- DISSYMMETRY** (Researches on PASTEUR's principle of the connection between molecular and physical), I, 1217.
- DORSMAN** (C.), H. KAMERLINGH ONNES and G. HOLST. Isothermals of di-atomic substances and their binary mixtures, XV, Vapour pressures of oxygen and critical point of oxygen and nitrogen, 950.
- DOYER** (LUCIE C.). Energy transformations during the germination of wheat-grains, 62.
- DROOGLEEVER FORTUYN** (A. B.), v. FORTUYN (A. B. DROOGLEEVER).
- DROSTE** (J.). On the field of a single centre in EINSTEIN's theory of gravitation, 998.

- EARTH (The mean radius of the), the intensity of gravity and the moon's parallax. 1291.  
 — (On isostasy, the moments of inertia and the compression of the). 1295.
- E H R E N F E S T (P.) and H. K A M E R L I N G H O N N E S. Simplified deduction of the formula from the theory of combinations which P L A N C K uses as the basis of his radiation-theory. 87<sup>0</sup>.  
 — On interference phenomena to be expected when RÖNTGEN rays pass through a di-atomic gas. 1184.  
 — On the kinetic interpretation of the osmotic pressure. 1241.
- E H R E N F E S T (T.)—A F A N A S S J E W A. Contribution to the theory of corresponding states. 840.
- E I N S T E I N's theory of gravitation (On the field of a single centre in). 998.
- E I N T H O V E N (On the theory of the string-galvanometer of). 784.
- E L A S T I C D E F O R M A T I O N (On the lowering of the freezing point in consequence of an). 732.
- E L E C T R I C C H A R G E and limit value of colloids. 623.
- E L E C T R O D E S (The effect of magnetisation of the) on the electromotive force. 745.
- E L E C T R O L Y T E S O L U T I O N S (Current potentials of) 615.
- E L E C T R O M A G N E T S (Modern), especially for surgical and metallurgic practice. 468.
- E L E C T R O M E T E R (A new) specially arranged for radio-active investigations. 659.
- E L E C T R O M O T I V E F O R C E (The effect of magnetisation of the electrodes on the). 745.
- E L I A S (G. J.). On the structure of the absorption lines  $D_1$  and  $D_2$ . 720.  
 — On the lowering of the freezing point in consequence of an elastic deformation. 732.  
 — The effect of magnetisation of the electrodes on the electromotive force. 745.
- E N D - P O I N T S (On critical) and the system ethane-naphtalene. 1095.
- E N E R G Y - S U R F A C E (The temperature-coefficients of the free) of liquids at temperatures from  $-80^\circ$  C. to  $1650^\circ$  C. I. 329. II. 365. III. 386. IV. 395. V. 405. VI. 416. VII. 555. VIII. 571.
- E N E R G Y - T R A N S F O R M A T I O N S during the germination of wheat-grains. 62.
- E N T R O P Y C O N S T A N T (Theoretical determination of the) of gases and liquids. 1167.
- E Q U A T I O N O F S T A T E (The chemical constant and the application of the quantum theory by the method of the natural vibrations to the) of an ideal monatomic gas. 20.
- E Q U I L I B R I A (The application of the theory of allotropy to electromotive). II. 37. III. 680.  
 — in the system Pb—SO, the roasting reaction process. 703.  
 — in ternary systems. XV. 70. XVI. 169. XVII. 767. XVIII. 1260.
- E R R A T U M. 944. 1073. 1202.
- E R R O R S I N S P A C E (The theory of BRAVAIS, on) for polydimensional space with applications to correlation. (Continuation). 150.
- E T H A N E - N A P H T A L E N E (On critical end-points and the system). 1095.
- E U R O P E A N S E A S (On the relation between departures from the normal in the strength of the trade-winds in the Atlantic Ocean and those in the waterlevel and temperature in the Northern). 1147.
- E Y K M A N (C.) presents a paper of Dr. L. K. W O L F F : "On the formation of antibodies after injection of sensitized antigens". II. 318.

- FISHES (The physiology of the air-bladder of). 1088.
- FLOATING (The different ways of) of an homogeneous cube. 224.
- FLORES (On the tin of the island of). 474.
- FOLMER (MISS H.). A new electrometer, specially arranged for radio-active investigations. 659.
- FONTAINE SCHLUITER (J. J. DE LA). v. SCHLUITER (J. J. DE LA FONTAINE).
- FORTUYN (A. B. DROOGLEEVER). The decoloration of fuchsin-solutions by amorphous carbon. 1322.
- FRANCHIMONT (A. P. N.) presents a paper of Dr. R. A. WEERMAN: "Action of sodium hypochlorite on amides of  $\alpha$ -oxyacids". 1163.
- and H. J. BACKER. The coloration of some derivatives of Picrylmethylamide with alkalies. 647.
- $\alpha$ -sulpho-propionic acid and its resolution into optically active isomerides. 653.
- FREEZING POINT (On the lowering of the) in connection of an elastic deformation. 732.
- FREQUENCIES (The treatment of) of directed quantities. 586.
- FRESNEL'S coefficient (On) for light of different colours. 445.
- FUCHSIN-SOLUTIONS (The decoloration of) by amorphous carbon. 1322.
- FUNCTIONS of HERMITE (On the). 1<sup>st</sup> part. 139.
- GALLÉ (P. H.). On the relation between departures from the normal in the strength of the trade-winds of the Atlantic Ocean and those in the waterlevel and temperature in the Northern European seas. 1147.
- GAS (The chemical constant and the application of the quantum theory by the method of the natural vibrations to the equation of state of an ideal monatomic). 20.
- (On interference phenomena to be expected when Röntgen rays pass through a di-atomic). 1184.
- GASES (The diffusion-coefficient of) and the viscosity of gas-mixtures. 1068.
- (Theoretical determination of the entropy constant of) and liquids. 1167.
- GAS EQUILIBRIA (On) and a test of Prof. v. D. WAALS JR.'s theorem. I. 695. II. 1011.
- GAS-LAWS (The influence of the hydration and of the deviations from the ideal) in aqueous solutions of salts on the solidifying and the boiling points. 1036.
- GAS-MIXTURES (The diffusion-coefficient of gases and the viscosity of). 1068.
- GELS (On the behaviour of) towards liquids and the vapours thereof. II. 92.
- Geodesy. H. G. VAN DE SANDE BAKHUYZEN, N. WILDEBOER and J. W. DIEPERINK: "Comparison of the measuring bar used in the base-measurement at Stroe, with the Dutch Metre No. 27". 300.
- H. G. VAN DE SANDE BAKHUYZEN: "Comparison of the platinum-iridium Metre No. 27 with the international Metre M as derived from the measurements by the Metre-Commission in 1879 and 1880, and a preliminary determination of the length of the measuring-bar of the French base-apparatus in international metres". 311.
- Geology. H. A. BROUWER: "On the granitic area of Rokan (Middle-Sumatra) and on contact-phenomena in the surrounding schists". 1190.
- Geophysics. J. P. VAN DER STOK: "The treatment of frequencies of directed quantities". 586.

- Geophysics.** P. H. GALLÉ: "On the relation between departures from the normal in the strength of the trade-winds of the Atlantic Ocean and those in the waterlevel and temperature in the Northern European seas". 1147.
- GEOTROPIC REACTIONS** (On the mutual influence of phototropic and) in plants. 1278.
- GERMINATION** (Energy transformations during the) of wheat-grains. 62.
- GRANITIC AREA** (On the) of Rokan (Middle-Sumatra) and on contact-phenomena in the surrounding schists. 1190.
- GRAVITATION** (On the field of a single centre in EINSTEIN'S theory of). 998.
- GRAVITY** (The mean radius of the earth, the intensity of) and the moon's parallax. 1291.
- GUMMOSIS** in the fruit (of the Almond and the Peachalmond as a process of normal life. 810.
- HAGA (H.)** presents a paper of Miss H. J. FOLMER: "A new electrometer, especially arranged for radio-active investigations". 659.
- presents a paper of Prof. F. M. JAEGER: "On a new phenomenon accompanying the diffraction of Röntgenrays in birefringent crystals". 1204.
- and F. M. JAEGER. On the real symmetry of cordierite and apophyllite. 430.
- HAMBURGER (H. J.)** presents a paper of Dr. E. LAQUEUR: "On the survival of isolated mammalian organs with automatic function". 270.
- presents a paper of Prof. A. A. HYMANS VAN DEN BERGH and J. J. DE LA FONTAINE SCHLUITER: "The identification of traces of bilirubin in albuminous fluids". 807.
- Phagocytes and respiratory centre. 1325.
- HEART-RHYTHM** (On the). 1075. II. 1135.
- HELDERMAN (W. D.)** and ERNST COHEN. The allotropy of cadmium. II. 54. III. 122. IV. 638. V. 1050.
- The allotropy of zinc. II. 59.
- The allotropy of copper. II. 60.
- The allotropy of lead. I. 822. Note. 1055.
- The metastability of the metals in consequence of allotropy and its significance for Chemistry, Physics and Technics. IV. 1238.
- HELIUM** (Further experiments with liquid). I. 12. 278. K. 283. L. 514. N. 520. M. 760.
- HERMITE** (On the functions of). 1<sup>st</sup> part. 139.
- and ABEL'S polynomia (On). 192.
- HOF (K.)** and H. KAMERLINGH ONNES. Further experiments with liquid helium. N. 520.
- HOLLEMAN (A. F.)** presents a paper of Dr. L. K. WOLFF and Dr. E. H. BÜCHNER: "On the behaviour of gels towards liquids and the vapours thereof. II. 92.
- presents a paper of Prof. J. BÖESEKEN: "On catalyse". 546.
- The nitration of the mixed dihalogen benzenes. 846.
- presents a paper of Prof. J. BÖESEKEN and W. D. COHEN: "The reduction of aromatic ketones. III. Contribution to the knowledge of the photochemical phenomena". 849.
- The replacement of substituents in benzene derivatives. 1027.
- presents a paper of Dr. C. H. SLUITER: "The influence of the hydration and

- of the deviations from the ideal gas-laws in aqueous solutions of salts on the solidifying and the boiling points". 1036.
- HOLLEMAN (A. F.) presents a paper of Miss ADA PRINS: „On critical end-points and the system ethane-naphthalene". 1095.
- HOLST (G.) and H. KAMERLINGH ONNES. The measurement of very low temperatures. XXIV. The hydrogen and helium thermometers of constant volume down to the freezing point of hydrogen compared with each other and with the platinum-resistance thermometer. 501.
- On the electrical resistance of pure metals. IX. 508.
- Further experiments with liquid helium. M. 760.
- H. KAMERLINGH ONNES and C. DORSMAN. Isothermals of di-atomic substances and their binary mixtures. XV. Vapour pressures of oxygen and critical point of oxygen and nitrogen. 950.
- HOOGEWERFF (S.) presents a paper of Prof. W. REINDERS: "Equilibria in the system Pb-S-O, the roasting reactionprocess. 703.
- HULSHOF (H.). On the thermodynamic potential as a kinetic quantity. 1st part. 85.
- HYDRATION (The influence of the) and of the deviations from the ideal gas-laws in aqueous solutions of salts on the solidifying and the boiling points. 1036.
- HYDROGEN (Measurements of isotherms of) at 20° C. and 15.5° C. 203.
- (Measurements on the capillarity of liquid). 528.
- HYDROGEN ISOTHERMS (The) of 20° C. and of 15.5° C. between 1 and 2200 atms. 217.
- Hydrostatics.** D. J. KORTEWEG: "The different ways of floating of an homogeneous cube". 224.
- HYMANS VAN DEN BERGH (A. A.) and J. J. DE LA FONTAINE SCHLUITER. The identification of traces of bilirubin in albuminous fluids. 807.
- INERTIA (On isostasy, the moments of) and the compression of the earth. 1295.
- INNERVATION (On the termination of the efferent nerves in plain muscle-cells and its bearing on the sympathetic (accessory)) of the striated muscle-fibre. 982.
- INTEGRAL EQUATIONS (On some). 286.
- INTEGRAL-FORMULA (On an) of STIELTJES. 829.
- INTERFERENCE-PHENOMENA (On) to be expected when Röntgen-rays pass through a di-atomic gas. 1184.
- INVOLUTION (A cubic) of the second class. 105.
- (A triple) of the third class. 134.
- ISOMERIDES ( $\alpha$ -Sulpho-propionic acid and its resolution into optically active). 653.
- ISOPRENE (A crystallized compound of) with sulphur dioxide. 585.
- ISOSTASY (On), the moments of inertia and the compression of the earth. 1295.
- ISOTHERMALS of di-atomic substances and their binary mixtures. XV. Vapour pressures of oxygen and critical point of oxygen and nitrogen. 950. XVI. Vapour-pressures of nitrogen between the critical point and the boiling point. 959.
- of monatomic substances and their binary mixtures. XVI. 275.
- ISOTHERMS (The hydrogen) of 20° C. and of 15.5° C. between 1 and 2200 atms. 217.
- of hydrogen (Measurements of) at 20° C. and 15.5° C. 203.

- JAEGER (F. M.). The temperature-coefficients of the free surface-energy of liquids at temperatures from  $-80^{\circ}$  C. to  $1650^{\circ}$  C. I. 329. V. 405. VI. 416. VII. 555. VIII. 571.
- On a new phenomenon accompanying the diffraction of Röntgenrays in birefringent crystals. 1204.
- Researches on PASTEUR's principle of the connection between molecular and physical dissymmetry. I. 1217.
- and H. HAGA. On the real symmetry of cordierite and apophyllite. 430.
- and JUL. KAHN. The temperature coefficients of the free surface-energy of liquids at temperatures from  $-80^{\circ}$  C. to  $1650^{\circ}$  C. IV. 395.
- and ANT. SIMEK. Studies in the field of silicate-chemistry. II. 239. III. 251.
- and M. J. SMIT. The temperature-coefficients of the free surface energy of liquids at temperatures from  $-80^{\circ}$  C. to  $1650^{\circ}$  C. II. 365. III. 386.
- JONG (A. W. K. DE). Action of sunlight on the cinnamic acids. 1274.
- JUPITER (The figure of the planet). 1047.
- KAHN (JUL.) and F. M. JAEGER. The temperature-coefficients of the free surface-energy of liquids at temperatures from  $-80^{\circ}$  C. to  $1650^{\circ}$  C. IV. 395.
- KAMERLINGH ONNES (H.). v. ONNES (H. KAMERLINGH).
- KAPPERS (C. U. ARIËNS) and P. RÖTHIG. Further contributions to our knowledge of the brain of *Myxine glutinosa*. 2.
- KAPTEYN (J. C.) presents a paper of Prof. M. J. VAN UVEN: "The theory of BRAVAIS (on errors in space) for polydimensional space, with applications to correlation". Continuation. 150.
- KAPTEYN (W.). On the functions of HERMITE. 1<sup>st</sup> part. 139.
- presents a paper of Dr. N. G. W. H. BEEGER: "On HERMITE's and ABEL's polynomia". 192.
- On some integral equations. 286.
- presents a paper of Prof. M. J. VAN UVEN: "The theory of the combination of observations and the determination of the precision, illustrated by means of vectors". 490.
- KEESOM (W. H.). The chemical constant and the application of the quantum theory by the method of the natural vibrations to the equation of state of an ideal monatomic gas. 20.
- On the matter in which the susceptibility of paramagnetic substances depends on the density. 110.
- and H. KAMERLINGH ONNES. The specific heat at low temperatures. I. Measurements on the specific heat of lead between  $14^{\circ}$  and  $80^{\circ}$  K. and of copper between  $15^{\circ}$  and  $22^{\circ}$  K. 894.
- KETONES (The reduction of aromatic). III. Contribution to the knowledge of the photochemical phenomena. 849.
- KINETIC INTERPRETATION (On the) of the osmotic pressure. 1241.
- KINETIC QUANTITY (On the thermodynamic potential as a). 1<sup>st</sup> part. 85.
- KLUYVER (J. C.). On an integral formula of STIELTJES. 829.

- KOHNSTAMM (PH.) and K. W. WALSTRA. Measurements of isotherms of hydrogen at 20° C. and 15°·5 C. 203.
- KORTEWEG (D. J.). The different ways of floating of an homogeneous cube. 224.
- KRUYT (H. R.). Current potentials of electrolyte solutions. 615.  
 — Electric charge and limit value of colloids. 623.  
 — and JAC. VAN DER SPEK. The connection between the limit value and the concentration of arsenic trisulphide sols. 1158.
- KUENEN (J. P.). On the measurement of the capillary pressure in a soap-bubble. 946.  
 — The diffusion-coefficient of gases and the viscosity of gas-mixtures. 1068.
- KUIPERS JR. (K.). The physiology of the air-bladder of fishes. 1088.
- KUYPERS (H. A.) and H. KAMERLINGH ONNES. Measurements on the capillarity of liquid hydrogen. 528.
- LAAR (J. J. VAN). A new relation between the critical quantities and on the unity of all substances in their thermic behaviour. 451.  
 — Some remarks on the values of the critical quantities in case of association. 598.  
 — On apparent thermodynamic discontinuities in connection with the value of the quantity  $b$  for infinitely large volume. 606.  
 — The calculation of the molecular dimensions from the supposition of the electric nature of the quasi-elastic atomic forces. 877.
- LAQUEUR (E.). On the survival of isolated mammalian organs with automatic function. 270.
- LEAD (The allotropy of). I. 822. Note. 1055.  
 — (Measurements on the specific heat of) between 14° and 80° K. and of copper between 15° and 22° K. 894.
- LIGHT (On FRESNEL's coefficient for) of different colours. 445.
- LIMIT VALUE (Electric charge and) of colloids. 623.  
 — (The connection between the) and the concentration of arsenic trisulphide sols. 1158.
- LIQUIDS (On the behaviour of gels towards) and the vapours thereof. II. 92.  
 — (Theoretical determination of the entropy constant of gases and). 1167.  
 — (The temperature-coefficients of the free energy-surface of) at temperatures from -80° C. to 1650° C. I. 329. II. 365. III. 389. IV. 395. V. 405. VI. 416. VII. 555. VIII. 571.
- LORENTZ (H. A.) presents a paper of Dr. J. J. VAN LAAR: "A new relation between the critical quantities and on the unity of all substances in their thermic behaviour". 451.  
 — presents a paper of Dr. J. J. VAN LAAR: "Some remarks on the values of the critical quantities in case of association". 598.  
 — presents a paper of Dr. J. J. VAN LAAR: "On apparent thermodynamic discontinuities in connection with the value of the quantity  $b$  for infinitely large volume". 606.  
 — presents a paper of Dr. G. J. ELIAS: "On the structure of the absorption lines  $D_1$  and  $D_2$ ". 720.

- LORENTZ (H. A.) presents a paper of Dr. G. J. ELIAS: "On the lowering of the freezing point in consequence of an elastic deformation". 732.
- presents a paper of Dr. G. J. ELIAS: "The effect of magnetisation of the electrodes on the electromotive force". 745.
- presents a paper of Dr. L. S. ORNSTEIN: "On the theory of the string galvanometer of EINTHOVEN". 784.
- presents a paper of Dr. L. S. ORNSTEIN and Dr. F. ZERNIKE: "Accidental deviations of density and opalescence at the critical point of a single substance". 793.
- presents a paper of Mrs. T. EHRENFEST—AFANASSJEWA: "Contribution to the theory of corresponding states". 840.
- presents a paper of Dr. J. J. VAN LAAR: "The calculation of the molecular dimensions from the supposition of the electric nature of the quasi-elastic atomic forces". 877.
- presents a paper of Mr. J. DROSTE: "On the field of a single centre in EINSTEIN's theory of gravitation". 998.
- presents a paper of Mr. H. TETRODE: "Theoretical determination of the entropy constant of gases and liquids". 1167.
- presents a paper of Prof. P. EHRENFEST: "On interference-phenomena to be expected when RÖNTGEN rays pass through a di-atomic gas". 1184.
- presents a paper of Prof. P. EHRENFEST: "On the kinetic interpretation of the osmotic pressure". 1241.
- LUNAR PERIGEE (The motions of the) and node and the figure of the moon. 1309.
- MAGNETISATION (The effect of) of the electrodes on the electromotive force. 745.
- MAMMALIAN ORGANS (On the survival of isolated) with automatic function. 270.
- Mathematics.** JAN DE VRIES: "A cubic involution of the second class". 105.
- JAN DE VRIES: "A triple involution of the third class". 134.
- W. KAPTEYN: "On the functions of HERMITE". 3th part. 139.
- M. J. VAN UVEN: "The theory of BRAVAIS (on errors in space) for polydimensional space with applications to correlation". (Continuation). 150.
- M. J. VAN UVEN: "Combination of observations with and without conditions and determination of the weights of the unknown quantities, derived from mechanical principles". 157.
- N. G. W. H. BEEGER: "On HERMITE's and ABEL's polynomia". 192.
- W. KAPTEYN: "On some integral equations". 286.
- M. J. VAN UVEN: "The theory of the combination of observations and the determination of the precision, illustrated by means of vectors". 490.
- J. C. KLUYVER: "On an integral formula of STIELTJES". 829.
- JAN DE VRIES: "Characteristic numbers for nets of algebraic curves". 935.
- JAN DE VRIES: "Characteristic numbers for a triple infinite system of algebraic plane curves". 1055.
- JAN DE VRIES: "Systems of circles determined by a pencil of conics". 1107.
- W. VAN DER WOUDE: "On NÖTHER's theorem". 1245.
- JAN DE VRIES: "A bilinear congruence of rational twisted quintics". 1250.

- Mathematics.** JAN DE VRIES: "Some particular bilinear congruences of twisted cubics". 1256.
- MATHIAS (E.), H. KAMERLINGH ONNES and C. A. CROMMELIN. The rectilinear diameter of nitrogen. 953.
- MEASUREMENT (The) of very low temperatures. XXIV. The hydrogen and helium thermometers of constant volume, down to the freezing point of hydrogen compared with each other and with the platinum-resistance thermometer. 501.
- MEASUREMENTS on the capillarity of liquid hydrogen. 528.
- of isotherms of hydrogen at  $21^{\circ}$  C. and  $15^{\circ}$  C. 203.
- on the specific heat of lead between  $14^{\circ}$  and  $80^{\circ}$  K. and of copper between  $15^{\circ}$  and  $22^{\circ}$  K. 894.
- MEASURING BAR (Comparison of the) used in the base measurement at Stree with the Dutch Metre No. 27. 300.
- (Comparison of the Dutch platinum-iridium Metre No. 27 with the international Metre *M* as derived from the measurements by the Dutch Metre-Commission in 1879 and 1880, and a preliminary determination of the length of the) of the French base-apparatus in international metres. 311.
- MECHANICAL PRINCIPLES (Combination of observations with and without conditions and determination of the weights of the unknown quantities derived from). 157.
- METALS (The metastability of) in consequence of allotropy, and its significance for Chemistry, Physics and Technics. 200. III. 926. IV. 1238.
- (On the electrical resistance of pure). IX. 508.
- METASTABILITY (The) of metals in consequence of allotropy and its significance for Chemistry, Physics and Technics. 200. III. 926. IV. 1238.
- METHYLAMINE (On the interaction of ammonia and) on 2, 3, 4-trinitrodimethylaniline. 1034.
- METRE No. 27 (Comparison of the Dutch platinum-iridium) with the international metre *M* as derived from the measurements by the Dutch Metre-Commission in 1879 and 1880, and a preliminary determination of the length of the measuring bar of the French baseapparatus in international metres. 311.
- Mineralogy.** H. HAGA and F. M. JAEGER: "On the real symmetry of cordierite and apophyllite". 430.
- C. E. A. WICHMANN: "On the tin of the island of Flores". 474.
- MOLECULAR DIMENSIONS (The calculation of the) from the supposition of the electric nature of the quasi-elastic atomic forces. 877.
- MOLENGRAAFF (G. A. F.) presents a paper of Dr. H. A. BROUWER: "On the granitic area of Rokan (Middle-Sumatra) and on contact-phenomena in the surrounding schists". 1190.
- MOON (The motions of the lunar perigee and node and the figure of the). 1309.
- MOON'S PARALLAX (The mean radius of the earth, the intensity of gravity and the). 1291.
- MUSCLE-CELLS (On the termination of the efferent nerves in plain) and its bearing on the sympathetic (accessory) innervation of the striated muscle-fibre. 982.
- MUSCULAR FIBRE (On the mode of attachment of the) to its tendonfibres in the striated muscles of the vertebrates. 989.

- MYXINE GLUTINOSA (Further contributions to our knowledge of the brain of). 2.
- NERVE-DISTRIBUTION (On the) in the trunk-dermatoma. 632.
- NERVES (On the termination of the efferent) in plain muscle cells and its bearing on the sympathetic (accessory) innervation of the striated muscle-fibre. 982.
- NETS (Characteristic numbers for) of algebraic curves. 935.
- NITRATION (The) of the mixed dihalogen benzenes. 846.
- NITROGEN (Vapour pressures of oxygen and critical point of oxygen and). 950.  
 — (The rectilinear diameter of). 953.  
 — (Vapour pressures of) between the critical point and the boiling point. 959.
- NÖTHER'S theorem (On). 1245.
- OCCCLUSION (A case of) of the arteria cerebelli posterior inferior. 914.
- ONNES (H. KAMERLINGH). Further experiments with liquid helium. J. 12.  
 278. K. 283. L. 514.  
 — presents a paper of Dr. W. H. KEESOM: "The chemical constant and the application of the quantum-theory by the method of the natural vibrations to the equation of state of an ideal monatomic gas". 20.  
 — presents a paper of Dr. W. H. KEESOM: "On the matter in which the susceptibility of paramagnetic substances depends on the density". 110.  
 — presents a paper of Dr. C. A. CROMMELIN: "Isothermals of monatomic substances and their binary mixtures". XVI. 275.  
 — presents a paper of Dr. C. A. CROMMELIN: "Isothermals of di-atomic substances and their binary mixtures". XVI. 959.  
 — C. DORSMAN and G. HOLST. Isothermals of di-atomic substances and their binary mixtures. XV. Vapour pressures of oxygen and critical point of oxygen and nitrogen. 950.  
 — and P. EHRENFEST. Simplified deduction of the formula from the theory of combinations which PLANCK uses as the basis of his radiation theory. 870.  
 — and K. HOF. Further experiments with liquid helium. N. 520.  
 — and G. HOLST. The measurement of very low temperatures. XXIV. The hydrogen and helium thermometers of constant volume down to the freezing point of hydrogen compared with each other and with the platinum-resistance thermometer. 501.  
 — On the electrical resistance of pure metals. IX. 508.  
 — Further experiments with liquid helium. M. 760.  
 — and W. H. KEESOM. The specific heat at low temperatures. I. Measurements on the specific heat of lead between 14° and 80° K. and of copper between 15° and 22° K. 894.  
 — and H. A. KUYPERS. Measurements on the capillarity of liquid hydrogen. 528.  
 — E. MATHIAS and C. A. CROMMELIN. The rectilinear diameter of nitrogen. 953.
- OPALESCEANCE (Accidental deviations of density and) at the critical point of a single substance. 793.
- ORNSTEIN (L. S.). On the theory of the stringgalvanometer of EINTHOVEN. 784.  
 — and F. ZERNIKE. Accidental deviations of density and opalescence at the critical point of a single substance. 793.

- OSMOTIC PRESSURE (On the kinetic interpretation of the). 1241.
- OXYGEN (Vapour pressures of) and critical point of oxygen and nitrogen. 950.
- PARAMAGNETIC SUBSTANCES (On the matter in which the susceptibility of) depends on the density. 110.
- PASTEUR'S principle (Researches on) of the connection between molecular and physical dissymmetry. I. 1217.
- PEACHALMOND (Gummosis in the fruit of the Almond and the) as a process of normal life. 810.
- Petrography.** A. WICHMANN: "On some rocks of the island of Taliabu (Sula islands). 226.
- PHAGOCYTES and respiratory centre. 1325.
- PHOSPHORUS (On the vapour pressure lines of the system). II. 678. III. 962.  
— (Further particulars concerning the system). 973.
- PHOTOCHEMICAL phenomena (Contribution to the knowledge of the). 849.
- PHOTOTROPIC and geotropic reactions (On the mutual influence of) in plants. 1278.
- Physics.** H. KAMERLINGH ONNES: "Further experiments with liquid helium". J. 12. 278. K. 283. L. 514. N. 520. M. 760.  
— W. H. KEESOM: "The chemical constant and the application of the quantum-theory by the method of the natural vibrations to the equation of state of an ideal monatomic gas". 20.  
— H. HULSHOF: "On the thermodynamic potential as a kinetic quantity". 1st part. 85.  
— W. H. KEESOM: "On the manner in which the susceptibility of paramagnetic substances depends on the density". 110.  
— PH. KOHNSTAMM and K. W. WALSTRA: "Measurement of isotherms of hydrogen at 20° C. and 15°5 C." 203.  
— K. W. WALSTRA: "The hydrogen isotherms of 20° C. and of 15°5 C. between 1 and 2200 atm." 217.  
— C. A. CROMMELIN: "Isothermals of monatomic substances and their binary mixtures". XVI. 275.  
— P. ZEEMAN: "FRESNEL'S coefficient for light for different colours". 1st part. 445.  
— J. J. VAN LAAR: "A new relation between the critical quantities and on the unity of all substances in their thermic behaviour". 451.  
— H. DU BOIS: "Modern electromagnets, especially for surgical and metallurgic practice". 468.  
— H. KAMERLING ONNES and G. HOLST: "On the measurement of very low temperatures. XXIV. The hydrogen and helium thermometers of constant volume, down to the freezing-point of hydrogen compared with each other and with the platinum resistance thermometer". 501.  
— H. KAMERLINGH ONNES and G. HOLST: "On the electrical resistance of pure metals etc.". IX. 508.  
— H. KAMERLINGH ONNES and H. A. KUYPERS: "Measurements on the capillarity of liquid hydrogen". 528.  
— J. J. VAN LAAR: "Some remarks on the values of the critical quantities in case of association". 598.

- Physics. J. J. VAN LAAR: "On apparent thermodynamic discontinuities in connection with the value of the quantity  $b$  for infinitely large volume". 606.
- Miss H. J. FOLMER: "A new electrometer, especially arranged for radio-active investigations". 659.
- G. J. ELIAS: "On the structure of the absorptionlines  $D_1$  and  $D_2$ ". 720.
- G. J. ELIAS: "The lowering of the freezing point in consequence of an elastic deformation". 732.
- G. J. ELIAS: "The effect of magnetisation of the electrodes on the electromotive force". 745.
- L. S. ORNSTEIN: "On the theory of the string-galvanometer of EINTHOVEN". 784.
- L. S. ORNSTEIN and F. ZERNIKE: "Accidental deviations of density and opalescence at the critical point of a single substance". 793.
- F. E. C. SCHEFFER: "On unmixing in a binary system for which the three phase pressure is greater than the sum of the vapour tensions of the two components". 834.
- Mrs. T. EHRENFEST—AFANASSJEWA: "Contribution to the theory of corresponding states". 840.
- P. EHRENFEST and H. KAMERLINGH ONNES: "Simplified deduction of the formula from the theory of combinations which PLANCK uses as the basis of his radiationtheory". 870.
- H. DU BOIS: "The universality of the ZEEMAN-effect with respect to the STARK-effect in canal-rays". 873.
- J. J. VAN LAAR: "The calculation of the molecular dimensions from the supposition of the electric nature of the quasi-elastic atomic forces". 877.
- W. H. KEESOM and H. KAMERLINGH ONNES: "The specific heat at low temperatures. I. Measurements on the specific heat of lead between  $14^\circ$  and  $80^\circ$  K. and of copper between  $15^\circ$  and  $22^\circ$  K." 894.
- J. P. KUENEN: "On the measurement of the capillary pressure in a soap-bubble". 946.
- H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST: "Isothermals of di-atomic substances and their binary mixtures. XV. Vapour pressures of oxygen and critical point of oxygen and nitrogen". 950.
- E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN: "The rectilinear diameter of nitrogen". 953.
- C. A. CROMMELIN: "Isothermals of di-atomic substances and their binary mixtures. XVI. Vapour pressures of nitrogen between the critical point and the boiling point". 959.
- J. DROSTE: "On the field of a single centre in EINSTEIN's theory of gravitation". 998.
- J. P. KUENEN: "The diffusion coefficient of gases and the viscosity of gas-mixtures". 1068.
- H. TETRODE: "Theoretical determination of the entropy constant of gases and liquids". 1167.

- Physics.** P. EHRENFEST: "On interference phenomena to be expected when Röntgen rays pass through a di-atomic gas". 1184.
- F. M. JAEGER: "On a new phenomenon accompanying the diffraction of Röntgen rays in birefringent crystals". 1204.
- P. EHRENFEST: "On the kinetic interpretation of the osmotic pressure". 1241.
- Physiology.** E. LAQUEUR: "On the survival of isolated mammalian organs with automatic function". 270.
- L. K. WOLFF: "On the formation of antibodies after injection of sensitized antigens". II. 318.
- G. VAN RIJNBEEK: "On the nerve-distribution in the trunk-dermatoma". 632.
- A. A. HYMANS VAN DEN BERGH and J. J. DE LA FONTAINE SCHLUITER: "The identification of traces of bilirubin in albuminous fluids". 807.
- I. K. A. WERTHEIM SALOMONSON: "Exaggeration of deep reflexes". 885.
- S. DE BGER: "On the heart-rhythm". 1075. II. 1135.
- A. B. DROOGLEEVER FORTUYN: "The decoloration of fuchsin-solutions by amorphous carbon". 1322.
- H. J. HAMBURGER: "Phagocytes and respiratory centre". 1325.
- PICRYLMETHYLAMIDE (The coloration of some derivatives of) with alkalis. 647.
- PLANCK (Simplified deduction of the formula from the theory of combinations which uses as the basis for his radiation theory. 870.
- PLANET Jupiter (The figure of the). 1047.
- PLANETS (On SEELIGER's hypothesis about the anomalies in the motion of the inner). 23.
- PLANTS (On the mutual influence of the phototropic and geotropic reactions in). 1278
- POLYNOMIA (On HERMITE's and ABEL's). 192.
- POSTMA (s.) and A. SMITS. The system Ammonia-water. 182.
- POTASSIUM (The allotropy of). I. 1115.
- POTASSIUM SULPHATE, potassium chlorid (The system: copper sulphate, copper chlorid) and water at 30°. 533.
- POTENTIAL (On the thermodynamic) as a kinetic quantity. 1st part. 85.
- POTENTIALS (Current) of electrolyte solutions. 615.
- PRECISION (The theory of the combination of observations and the determination of the), illustrated by means of vectors. 490.
- PRINS (Miss ADA). On critical end-points and the system ethane-naphthalene. 1095.
- PSEUDO-COMPONENTS (The metastable continuation of the mixed crystal series of) in connection with the phenomenon allotropy. II. 672.
- QUANTITY  $b$  (On apparent thermodynamic discontinuities in connection with the value of the) for infinitely large volume. 606.
- QUANTUM-THEORY (The chemical constant and the application of the) by the method of the natural vibrations to the equation of state of an ideal monatomic gas). 20.
- QUATERNARY SYSTEM  $KCl-CuCl_2-BaCl_2-H_2O$  (On the). 781.
- QUINTICS (A bilinear congruence of rational twisted). 1250.
- RADIATION THEORY (Simplified deduction of the formula from the theory of combinations which PLANCK uses as the basis for his). 870.

- RADIO-ACTIVE investigations (A new electrometer, specially arranged for). 659.
- REFLEXES (Exaggeration of deep). 885.
- REINDERS (W.). Equilibria in the system Pb-S-O, the roasting reaction process. 703.
- RESISTANCE (On the electrical) of pure metals. IX. 508.
- RESPIRATORY CENTRE (Phagocytes and). 1325.
- ROASTING REACTION PROCESS (Equilibria in the system Pb-S-O, the). 703.
- ROCKS (On some) of the island of Taliabu (Sula islands). 226.
- ROKAN (Middle-Sumatra) (On the granitic area of) and on contact phenomena in the surrounding schists. 1190.
- ROMBURGH (P. VAN) presents a paper of Prof. F. M. JAEGER and Dr. ANT. SIMEK: "Studies in the field of silicate-chemistry". II. 239. III. 251.
- presents a paper of Prof. F. M. JAEGER: "The temperature-coefficients of the free surface-energy of liquids at temperatures from  $-80^{\circ}$  to  $1650^{\circ}$  C." I. 329. II. 365. III. 386. IV. 395. V. 405. VI. 416. VII. 555. VIII. 571.
- presents a paper of Mr. G. DE BRUIN: "A crystallized component of isoprene with sulphur dioxide". 585.
- presents a paper of Prof. F. M. JAEGER: "Researches on PASTEUR's principle of the connection between molecular and physical dissymmetry". I. 1217.
- presents a paper of Dr. A. W. K. DE JONG: "Action of sunlight on the cinnamic acids". 1274.
- and Miss D. W. WENSINK. On the interaction of ammonia and methylamine on 2,3,4-trinitrodimethylaniline. 1034.
- RÖNTGEN RAYS (On interference phenomena to be expected when) pass through a di-atomic gas. 1184.
- (On a new phenomenon accompanying the diffraction of) in birefringent crystals. 1204.
- RÜTHIG (P.) and C. U. ARIËNS KAPPERS. Further contributions to our knowledge of the brain of *Myxine glutinosa*. 2.
- RIJNBEEK (G. VAN). On the nerve-distribution of the trunk-dermatoma. 632.
- SALOMONSON (J. K. A. WERTHEIM). Exaggeration of deep reflexes. 885.
- presents a paper of Dr. S. DE BOER: "On the heart-rhythm". 1075. II. 1135.
- SALTS (The influence of the hydration and of the deviations from the ideal gas-laws in aqueous solutions of) on the solidifying and the boiling point. 1036.
- SANDE BAKHUYZEN (H. G. VAN DE), v. BAKHUYZEN (H. G. VAN DE SANDE).
- SCHEFFER (F. E. C.). On gas equilibria and a test of Prof. v. D. WAALS JR.'s theorem. I. 695. II. 1011.
- On unmixing in a binary system for which the three-phase pressure is greater than the sum of the vapour tensions of the two components. 834.
- SCHLUITER (J. J. DE LA FONTAINE) and A. A. HYMANS VAN DEN BERGH. The identification of traces of bilirubin in albuminous fluids. 807.
- SCHREINEMAKERS (F. A. H.). Equilibria in ternary systems. XV. 70. XVI. 169. XVII. 767. XVIII. 1260.
- and Miss W. C. DE BAAT. The system: copper sulphate, copper chlorid, potassium sulphate, potassium chlorid and water at  $30^{\circ}$  C. 533.

- SCHREINEMAKERS (F. A. H.) and Miss W. C. DE BAAT. On the quaternary system  $KCl-CuCl_2-BaCl_2-H_2O$ . 781.
- Compounds of the arsenious oxide, I. 1111.
- SEELIGER's hypothesis (On) about the anomalies in the motion of the inner planets. 23.
- (Remarks on Mr. WOLTJER's paper concerning). 33.
- SILICATE-CHEMISTRY (Studies in the field of). II. 239. III. 251.
- SIMEK (A. N. T.) and F. M. JAEGER. Studies in the field of silicate-chemistry. II. 239. III. 251.
- SITTER (W. DE) presents a paper of Mr. J. WOLTJER JR.: "On SEELIGER's hypothesis about the anomalies in the motion of the inner planets". 23.
- Remarks on Mr. WOLTJER's paper concerning SEELIGER's hypothesis. 33.
- The figure of the planet Jupiter. 1047.
- On the mean radius of the earth, the intensity of gravity and the moon's parallax. 1291.
- On isostasy, the moment of inertia and the compression of the earth. 1295.
- The motions of the lunar perigee and node and the figure of the moon. 1309.
- SLUITER (C. H.). The influence of the hydration and of the deviations from the ideal gas-laws in aqueous solutions of salts on the solidifying and the boiling-point. 1036.
- SMIT (M.) and F. M. JAEGER. The temperature-coefficients of the free-surface-energy of liquids at temperatures from  $-50^\circ C.$  to  $1650^\circ C.$  II. 365. III. 381.
- SMITS (A.). The metastable continuation of the mixed crystal series of pseudo-components in connection with the phenomenon allotropy. II. 672.
- and ATEN (A. H. W.). The application of the theory of allotropy to electro-motive equilibria. II. 37. III. 680.
- and S. C. BOKHORST. On the vapour pressure lines in the system phosphorus. II. 678. III. 962.
- Further particulars concerning the system phosphorus. 973.
- and S. POSTMA. The system ammoniawater. 182.
- SOAP-BUBBLE (On the measurement of the capillary pressure in a). 946.
- SODIUM-HYPOCHLORITE (Action of) on amides of  $\alpha$ -oxyacids. 1163.
- SPECIFIC HEAT (The) at low temperatures. I. Measurements on the specific heat of lead between  $14^\circ$  and  $80^\circ K.$  and of copper between  $15^\circ$  and  $22^\circ K.$  894.
- SPEK (J. A. C. VAN DER) and H. R. KRUYT. The connection between the limit value and the concentration of arsenic trisulphide sols. 1158.
- STARK-effect (The universality of the ZEEMAN-effect with respect to the) in canal-rays. 873
- STIELTJES (On an integral-formula of). 829.
- STOK (J. P. VAN DER). The treatment of frequencies of directed quantities. 586.
- presents a paper of Mr. P. H. GALLÉ: "On the relation between departures from the normal in the strength of the trade-winds in the Atlantic Ocean and those in the waterlevel and temperature in the Northern European seas." 1147.
- STRING-GALVANOMETER (On the theory of the) of EINTHOVEN. 784.
- STROE (Comparison of the measuring bar used in the base measurement at) with the Dutch Metre  $n^0$  27. 300.
- SUBSTANCES (Isothermals of monatomic) and their binary mixtures. XVI. 275.
- (Isothermals of di-atomic) and their binary mixtures. XV. 950. XVI. 959.

- SUBSTANCES (A new relation between the critical quantities and on the unity of all) in their thermic behaviour. 451.
- SUBSTITUENTS (The replacement of) in benzene derivatives. 1027.
- $\alpha$ -SULPHO-PROPIONIC ACID and its resolution into optically active isomerides. 653.
- SULPHUR DIOXIDE (A crystallized compound of isoprene with). 585.
- SUNLIGHT (Action of) on the cinnamic acids. 1274.
- SYSTEM *Pb-S-O* (Equilibria in the), the roasting reaction process. 703.
- (The) copper sulphate, copper chlorid, potassium sulphate, potassium chlorid and water at 30° C. 533.
  - (Characteristic numbers for a triply infinite) of algebraic plane curves. 1055.
  - ammonia—water (The). 182.
  - ethane—naphthalene (On critical endpoints and the). 1095.
  - phosphorus (On the vapour pressure lines in the). II. 673. III. 962.
  - phosphorus (Further particulars concerning the). 973.
- TALIABU (Sula islands) (On some rocks of the island of). 226.
- TEMPERATURE (On the relation between departures from the normal in the strength of the trade-winds of the Atlantic Ocean and those in the waterlevel and) in the Northern European seas. 1147.
- TEMPERATURE-COEFFICIENTS (The) of the free energy surface of liquids at temperatures from -80° C. to 1650° C. I. 329. II. 365. III. 386. IV. 395. V. 405. VI. 416. VII. 555. VIII. 571.
- TEMPERATURES (The measurement of very low). XXIV. The hydrogen and helium thermometers of constant volume down to the freezing point of hydrogen compared with each other and with the platinum-resistance thermometer. 501.
- (The specific heat at low). I. Measurements on the specific heat of lead between 14° and 80° K. and of copper between 15° and 22° K. 894.
- TENDONFIBRES (On the mode of attachment of the muscular fibre to its) in the striated muscles of the vertebrates. 989.
- TERNARY SYSTEMS (Equilibria in). XV. 70. XVI. 169. XVII. 767. XVIII. 1260.
- TETRODE (H.). Theoretical determination of the entropy constant of gases and liquids. 1167.
- THEORY of allotropy (The application of the) to electromotive equilibria. II. 37. III. 680.
- of BRAVAIS (The) (on errors in space) for polydimensional space with applications to correlation. (Continuation). 150.
  - (The) of the combination of observations and the determination of the precision, illustrated by means of vectors. 490.
  - of combinations (Simplified deduction of the formula from the) which PLANCK uses as the basis of his radiation theory. 870.
  - of corresponding states (Contribution to the). 840.
  - of gravitation (On the field of a single centre in EINSTEIN'S). 993.
- THERMOMETERS (The hydrogen and helium) of constant volume, down to the freezing point of hydrogen compared with each other, and with the platinum-resistance thermometer. 501.
- THREE-PHASE PRESSURE (On unmixing in a binary system for which the) is greater than the sum of the vapour tensions of the two components. 834.

- TIN (On the) of the island of Flores. 474.
- TRADE-WINDS (On the relation between departures from the normal in the strength of the) in the Atlantic Ocean and those in the waterlevel and temperature in the Northern European seas. 1147.
- TRINITRODIMETHYLANILINE (On the interaction of ammonia and methylamine on 2.3.4.-). 1034.
- TRUNK-DERMATOMA (On the nerve-distribution in the). 632.
- UNMIXING (On) in a binary system for which the three-phase pressure is greater than the sum of the vapour tensions of the two components. 834.
- UVEN (M. J. VAN). The theory of BRAVAIS (on errors in space) for polydimensional space with applications to correlation. (Continuation). 150.
- Combination of observations with and without conditions and determination of the weights of the unknown quantities, derived from mechanical principles. 157.
  - The theory of the combination of observations and the determination of the precision, illustrated by means of vectors. 490.
- VAGUS AREA (The) in Camelidae. 1119.
- VAPOUR PRESSURE LINES (On the) in the system phosphorus. II. 678. III. 962.
- VAPOUR PRESSURES of oxygen and critical point of oxygen and nitrogen. 950.
- of nitrogen between the critical point and the boiling point. 959.
- VAPOUR TENSIONS (On unmixing in a binary system for which the three-phase pressure is greater than the sum of the) of the two components. 834.
- VECTORS (The theory of the combination of observations and the determination of the precision, illustrated by means of). 490.
- VÉRMEULEN (H. A.). The vagus area in Camelidae. 1119.
- VERTEBRATES (On the mode of attachment of the muscular fibre to its tendonfibres in the striated muscles of the). 989.
- VISCOSITY of gas-mixtures (The diffusion-coefficient of gases and the). 1063.
- VRIES (JAN DE). A cubic involution of the second class. 105.
- A triple involution of the third class. 134.
  - presents a paper of Prof. M. J. VAN UVEN: "Combination of observations with and without conditions and determination of the weights of the unknown quantities, derived from mechanical principles". 157.
  - Characteristic numbers for nets of algebraic curves. 935.
  - Characteristic numbers for a triple infinite system of algebraic plane curves. 1055.
  - Systems of circles determined by a pencil of conics. 1107.
  - presents a paper of Dr. W. VAN DER WOUDE: "On NÖTHER's theorem". 1245.
  - A bilinear congruence of rational twisted quintics. 1250.
  - Some particular bilinear congruences of twisted cubics. 1256.
- WAALS (J. D. VAN DER) presents a paper of Prof. A. SMITS and Dr. A. H. W. ATEN: "The application of the theory of allotropy to electromotive equilibria". II. 37. III. 680.
- presents a paper of Dr. H. HULSHOF: "On the thermodynamic potential as a kinetic quantity", 1st. part. 85.
  - presents a paper of Prof. A. SMITS and S. POSTMA: "The system ammonia-water." 182.

- W A A L S (J. D. V A N D E R) presents a paper of Prof. PH. KOHNSTAMM and K. W. WALSTRA: "Measurements of isotherms of hydrogen at 20° C. and 15°5 C." 203.
- presents a paper of Mr. K. W. WALSTRA: "The hydrogen isotherms of 20° C. and of 15°5 C. between 1 and 2200 atm." 217.
- presents a paper of Prof. A. SMITS: "The metastable continuation of the mixed crystal series of pseudo-components in connection with the phenomenon allotropy". II. 672.
- presents a paper of Prof. A. SMITS and S. C. BOKHORST: "The vapour pressure lines of the system phosphorus". II. 678. III. 962.
- presents a paper of Dr. F. E. C. SCHEFFER: "On gas equilibria and a test of Prof. V A N D E R W A A L S Jr.'s formula". I. 695. II. 1011.
- presents a paper of Dr. F. E. C. SCHEFFER: "On unmixing in a binary system for which the three-phase pressure is greater than the sum of the vapour tensions of the components". 834.
- presents a paper of Prof. A. SMITS and S. C. BOKHORST: "Further particulars concerning the system phosphorus". 973.
- W A A L S J R.'s theorem (On gas equilibria and a test of Prof.). I. 695. II. 1011.
- W A L S T R A (K. W.). The hydrogen isotherms of 20° C. and of 15°5 C. between 1 and 2200 atm. 217.
- and PH. KOHNSTAMM. Measurements of isotherms of hydrogen at 20° C. and 15°5 C. 203.
- W A T E R (The system ammonia-). 182.
- (The system: copper sulphate, copper chlorid, potassium sulphate, potassium chlorid and) at 30°. 533.
- W A T E R L E V E L (On the relation between departures from the normal in the strength of the trade-winds in the Atlantic ocean and those in the) and temperature in the Northern European seas. 1147.
- W E B E R (M A X) presents a paper of Dr. K. KUIPER JR.: "The physiology of the air-bladder of fishes". 1088.
- W E E R M A N (R. A.). Action of sodium hypochlorite on amides of  $\alpha$ -oxyacids. 1163.
- W E I G H T S (Combination of observations with and without conditions and determination of the) of the unknown quantities, derived from mechanical principles. 157.
- W E N S I N K (Miss D. W.) and P. V A N R O M B U R G H. On the interaction of ammonia and methylamine on 2,3,4.-trinitrodimethylaniline. 1034.
- W E N T (F. A. F. C.) presents a paper of Miss LUCIE C. DOYER: "Energy transformations during the germination of wheat-grains". 62.
- presents a paper of Dr. C. E. B. BREMEKAMP: "On the mutual influence of phototropic and geotropic reactions in plants". 1278.
- W E R T H E I M S A L O M O N S O N (I. K. A.). v. S A L O M O N S O N (I. K. A. W E R T H E I M).
- W H E A T - G R A I N S (Energy transformations during the germination of). 62.
- W I C H M A N N (A.). On some rocks of the island of Taliabu (Sula islands). 226.
- On the tin of the island of Flores. 474.
- W I L D E B O E R (N.), J. G. DIEPERINK and H. G. V A N D E S A N D E B A K H U Y Z E N. Comparison of the measuring bar used in the base measurement at Stroe with the Dutch Metre No. 27. 300.

- WINKLER (C.) presents a paper of Prof. G. VAN RIJNBEEK: "On the nerve-distribution of the trunkdermatoma." 632.
- A case of occlusion of the arteria cerebelli posterior inferior. 914.
- WOLFF (L. K.). On the formation of antibodies after injection of sensitized antigens. II. 318.
- and E. H. BÜCHNER. On the behaviour of gels towards liquids and the vapours thereof. II. 92.
- WOLFF (S.) and ERNST COHEN. The allotropy of potassium. I. 1115.
- WOLTJER JR. (J.). On SEELIGER's hypothesis about the anomalies in the motion of the inner planets. 23.
- WOUDE (W. VAN DER). On NÖTHER's theorem. 1245.
- ZEEMAN (P.). On FRESNEL's coefficient for light of different colours. 445.
- ZEEMAN-effect (The universality of the) with respect to the STARK-effect in canal-rays. 873.
- ZERNIKE (F.) and L. S. ORNSTEIN. Accidental deviations of density and opalescence at the critical point of a single substance. 793.
- ZINC (The allotropy of). II. 59. III. 641.
- Zoology.** K. KUIPER JR.: "The physiology of the air-bladder of fishes." 1088.
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VOLUME XVII  
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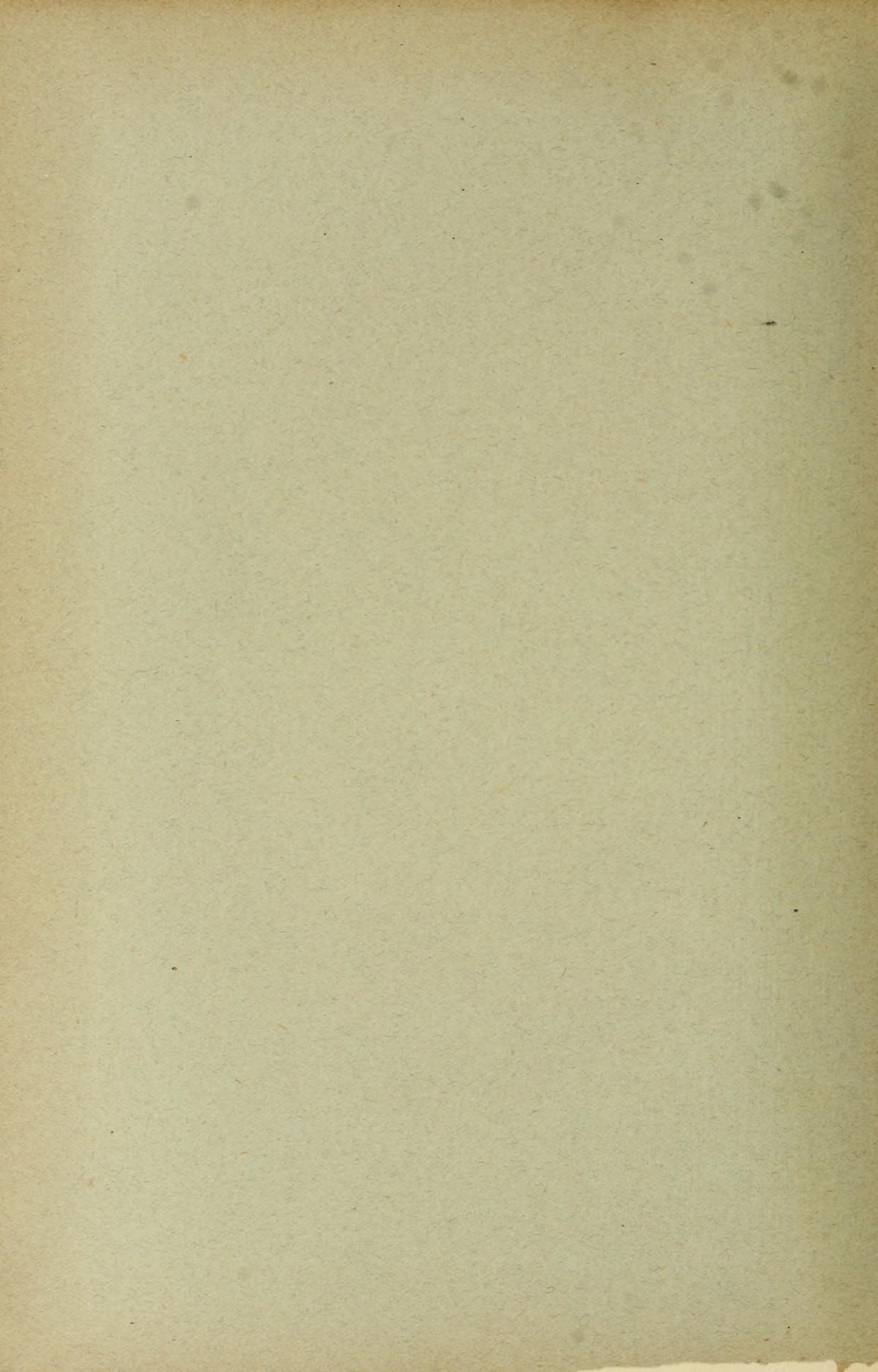


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