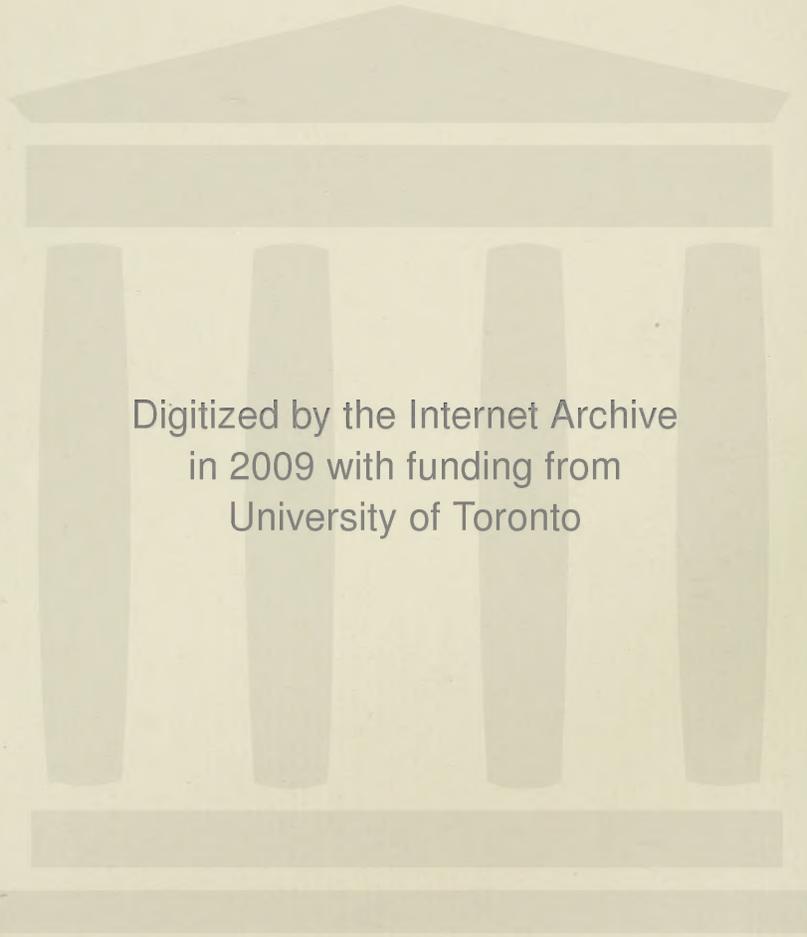


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# PROCEEDINGS

OF THE

SECTION OF SCIENCES.

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VOLUME VI.

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AMSTERDAM,  
JOHANNES MÜLLER.  
July 1904.

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(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige  
Afdeling van 30 Mei 1903 tot 23 April 1904. Dl. XII.)

E R R A T U M.

Page 644 line 36 for **chloride** read **chlorine**.  
» 647 » 24 » 7290 » 7920

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Koninklijke Akademie van Wetenschappen  
te Amsterdam.

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# PROCEEDINGS

OF THE

SECTION OF SCIENCES.

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VOLUME VI.

(1st PART.)

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AMSTERDAM,  
JOHANNES MÜLLER.  
December 1903.

(Translated from Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige  
Afdeeling van 30 Mei 1903 tot 28 November 1903. Dl. XII)

# C O N T E N T S.



		Page.
Proceedings of the Meeting of May 30	1908 . . . . .	1
» » » » June 27	» . . . . .	63
» » » » September 26	» . . . . .	171
» » » » October 31	» . . . . .	279
» » » » November 31	» . . . . .	327





KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING  
of Saturday May 30, 1903.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 30 Mei 1903, Dl. XII).

CONTENTS.

J. W. DITO: "The action of phosphorus on hydrazine". (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 1.

J. W. COMMELIN and ERNST COHEN: "The electromotive force of the DANIELL-cells". (Communicated by Prof. W. H. JULIUS), p. 4.

JAN DE VRIES: "On complexes of rays in relation to a rational skew curve", p. 12.

W. A. VERSLUYS: "The singularities of the focal curve of a curve in space". (Communicated by Prof. P. H. SCHOOTE), p. 17.

P. ZEEMAN and J. GEEST: "On the double refraction in a magnetic field near the components of a quadruplet", p. 19.

J. J. VAN LAAR: "The course of the melting-point-line of alloys (3.d communication). (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 21.

M. C. DEKLUYZEN and P. VERMAAT: "On the epithelium of the surface of the stomach". (Communicated by Prof. C. A. PEKELHARING), p. 30.

E. HEKMA: "On the liberation of trypsin from trypsin-zymogen". (Communicated by Prof. H. J. HAMBURGER), p. 34.

A. PASSEKOEK: "Some remarks on the reversibility of molecular motions". (Communicated by Prof. H. A. LORENTZ), p. 42.

C. A. J. A. OUDEMANS and C. J. KONING: "On a Sclerotinia hitherto unknown and injurious to the cultivation of Tobacco (*Sclerotinia Nicotianae* OUD. et KONING), p. 48 (with one plate).

J. E. VERSCHAFFELT: "Contributions to the knowledge of VAN DER WAALS'  $\psi$ -surface. VI. (part 3). The equations of state and the  $\psi$ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components". (Communicated by Prof. H. KAMERLINGH ONNES), p. 59.

The following papers were read:

**Chemistry.** — "*The action of phosphorus on hydrazine.*" By  
Mr. J. W. DITO. (Communicated by Prof. C. A. LOBRY DE BRUYN).  
(Communicated in the meeting of April 24, 1903.)

The last number of the *Berichte*<sup>1)</sup> contains a research on phosphorus by R. SCHENCK. Several of his observations quite corroborate those which have been announced some time ago<sup>2)</sup> and which were made

<sup>1)</sup> Ber. **36**. 979.

<sup>2)</sup> Recueil **18**. 297. (1899).

in 1900—1901, but the publication of which was postponed owing to other studies which are not yet complete.

In 1895 <sup>1)</sup> and also afterwards <sup>2)</sup> LOBRY DE BRUYN, in his studies on hydrazine, observed that yellow phosphorus in contact with aqueous hydrazine turns the solution first yellow, then dark brown and finally black. After some time brownish black amorphous flakes are deposited. As already stated, I submitted this reaction some years ago to a closer examination and studied it, both with aqueous and with anhydrous hydrazine.

I. If we introduce into vacuum tubes 16 gr.(=6 at.) yellow phosphorus and 5 c.c. of a concentrated 90 % (= 1 mol.) aqueous solution of hydrazine and allow these to be in contact for 1 or 2 months at the ordinary temperature the whole solidifies to a black amorphous mass in which a white well-crystallised substance is distributed. On opening the tubes a large quantity of hydrogen phosphide appears to be present. As preliminary experiments had shown that the white substance was soluble in absolute alcohol but not the black substances, the tubes were filled with absolute alcohol out of contact with the air, the black substance was freed from the white crystals by repeated washing with absolute alcohol and then dried over sulphuric acid in vacuum.

The crystalline product obtained on evaporating the alcohol, was particularly hygroscopic. The analysis agreed best with the assumption that it consisted of hydrazine phosphite. Found 30.4 % P and 12.3% N (this was determined in a nitrometer by means of vanadic acid) <sup>3)</sup>. If however notwithstanding the necessary precautions, the substance has attracted a good deal of moisture in the course of the different manipulations, there is a possibility of its being hydrazine hypophosphite <sup>4)</sup>.

The black mass is insoluble in alcohol, ether and carbon disulphide and free from excess of yellow phosphorus. It has an odour of hydrogen phosphide; in contact with the air it becomes moist and the black colour changes to yellow. It contains chemically combined hydrazine which, in company with a little hydrogen phosphide, is obtained on distilling with dilute sodium hydroxide and which could be identified by means of its dibenzaldehyde-derivative which melts at 93°.

<sup>1)</sup> Recueil **14**. 87.

<sup>2)</sup> Recueil **15**. 183.

<sup>3)</sup> HOFFMANN and KÜSPERT Ber. **31**. 64.

<sup>4)</sup> SABANEJEFF, Z. anorg. Ch. **20**. 21. (1899).

The black substance is strongly attacked by dilute nitric acid and also by bromine water. On heating at  $100^{\circ}$  in a current of dry hydrogen it loses weight continuously and the black colour changes to red.

On treatment with dilute acids it behaves exactly like the product isolated by SCHENCK from red phosphorus and ammonia<sup>1)</sup>. It is then converted into a light red amorphous powder whilst the solution appears to contain a salt of hydrazine. The red powder has the external appearance of red phosphorus but is distinguished from this by a more orange tinge and its behaviour towards alkalis. Ammonia and dilute soda or potash yield black products, which however on prolonged washing with water lose their feebly combined alkali and assume their original red color. The substance, therefore, behaves as a weak acid which forms black alkali salts which readily undergo hydrolysis.

Strong alkalis act energetically on the red substance with formation of hydrogen phosphide and a salt of hypophosphorous acid.

In the analysis of the black and the red substance the phosphorus was determined by means of dilute nitric acid (in sealed tubes) and with bromine water. The nitrogen determination was done volumetrically with bromine water in a current of carbon dioxide and the hydrogen by an elementary analysis.

The average result was 45.9 % P, 19.8 N and 5.5 % H; total 71.2; the balance may be taken as representing oxygen.

The red compound was free from nitrogen so that the black product appears to be the hydrazine derivative of the red substance.

The product dried in a desiccator in vacuo contained 91.7 % P and 1.1 % H<sup>2)</sup>.

2. If we place in a vacuum tube an excess of yellow phosphorus with free hydrazine  $N_2H_4$ , we also notice (although sooner than in the case of the aqueous solution) the formation of a black amorphous substance which in appearance quite resembles the product obtained from hydrated hydrazine. No white substance is of course formed, hardly any pressure is noticed and also little or no formation of hydrogen phosphide takes place. This gas, like the hydrazine phosphite, therefore owed its origin to the well-known reaction between phosphorus and a base.

<sup>1)</sup> That black compounds are also formed from liquefied ammonia and white phosphorus is shown by the experiments of GORE, Proc. Roy. Soc. **21**, 140. (1872), FRANKLIN and KRAUS, Amer. Ch. J. **20**, 820. (1898), and HUGOT, Ann. Chim. Phys. **21**, 28. (1900).

<sup>2)</sup> This figure is almost sure to be too high owing to the nature of the process (elementary analysis).

The black substance was washed with carbon disulphide and alcohol and dried in a desiccator in vacuo. Apparently it has absorbed oxygen during this operation for the analysis showed a deficit of about 13 %. We found: 78.5 % P, 1.9 % H and 6.5 % N.

When treated with dilute acids a red substance was again formed which in appearance and properties corresponded exactly with the one already described and contained the same amount of phosphorus [found, average 92 %]. The hydrazine has passed into the acid.

3. From the foregoing it follows that substances quite analogous to those formed by SCHENCK's (impure) red phosphorus and ammonia are generated directly from hydrazine and yellow phosphorus. Evidently, the black compounds which are formed from aqueous and anhydrous hydrazine are of a different nature; their investigation remains however very unsatisfactory, owing to their amorphous conditions and want of tests for purity, in addition to their instability towards washing-liquids. But it is pretty certain that the orange red product which both yield, when treated with acids, is a weak acid composed of phosphorus, hydrogen (and oxygen?)

Hydrazine is therefore capable of directly giving up hydrogen, not only to sulphur but also to phosphorus.

*Organic chem. Lab. University.*

*Amsterdam, April 1903.*

**Chemistry.** — "*The electromotive force of the DANIELL-cells.*" By Mr. J. W. COMMELIN and Prof. ERNST COHEN. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of April 24, 1903).

1. In the present state of our electro-chemical knowledge an exhaustive study of the electromotive force of the DANIELL-cell would have but little importance if it related to the use of this cell as a standard-cell, as we are now in possession of standard-cells which, if properly constructed, satisfy all requirements.

We have, nevertheless undertaken an exhaustive investigation of such a cell because J. CHAUDIER has published in the "*Comptes Rendus*"<sup>1)</sup> certain views which are entirely opposed to our modern theories on the origin of the electromotive force in cells of this kind.

<sup>1)</sup> 134, 277 (1902).

2. CHAUDIER gives the following form to the well-known formula of NERNST for the electromotive force:

$$E = KT \left( \log \frac{P}{p} - \log \frac{P_1}{p_1} \right) + T \frac{dE}{dT}.$$

This is evidently a mistake as the second term after the sign of equality does not belong to this formula but forms part of the well-known equation of GIBBS and VON HELMHOLTZ<sup>1)</sup>.

This mistake we may pass over. The following table contains CHAUDIER'S results which have been obtained by means of BOUTY'S method for the measurement of electromotive forces. His cells were constructed according to the scheme:

Copper	Copper sulphate solution saturated at 15° C.	Dilute solution of Zinc sulphate.	Zinc.
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3. The paper contains but few details of the manner in which the experiments were conducted: "l'élément DANIELL est constitué par deux vases en verre, contenant l'un la solution de sulfate de zinc, l'autre la solution de sulfate de cuivre; ces deux vases sont réunis par un siphon formé d'un tube de verre rempli de coton imbibé de la solution de sulfate de zinc dans l'une des branches, de la solution

TABLE I.

ZnSO <sub>4</sub> · 7H <sub>2</sub> O in 100 parts of water.	Elektromot. force (15° C.)	Coefficient of temperature.
0	1.0590 Volt	-0.0024
1/12	1.1138	-0.00015
1/6	1.1151	-0.00013
1/2	1.1368	+0.00005
1	1.1331	+0.00005
2	1.1263	+0.00003
4	1.1249	+0.00003
6	1.1208	+0.00016
10	1.1188	-0.00003
30	1.1054	-0.0002
60	1.1003	-0.0002
200 (saturated)	1.0902	-0.00026

<sup>1)</sup> CHAUDIER wrongly calls this equation, the equation of Lord KELVIN.

de sulfate de cuivre dans l'autre. Ce dispositif m'a paru donner des resultats plus constants que les autres."

It seems to us strange that the E. M. F. should be given to  $\frac{1}{10}$  millivolt. All authors who up to the present have made a study of the DANIELL-cell have pointed out how difficult it is to obtain constant values with such cells. For instance, the E. M. F. is in a high degree dependent on the nature of the copper or zinc electrode. For particulars in this direction we refer to the researches of ALDER WRIGHT<sup>1)</sup>.

In connection with the measurements under consideration the following table of FLEMING's will be found interesting:

*E. M. F. of a certain DANIELL-cell.*

COPPER, perfectly pure, unoxidised	1.072 Volt
"  slightly oxidised, brown spots	1.076 "
"  more oxidised	1.082 "
"  covered with dark brown oxide film	1.089 "
"  cleaned, replated with fresh pinkish electro-surface	1.072 "

4. In repeating CHAUDIER's measurements it is of the greatest importance to have the determinations mutually comparable; errors caused by an unlike nature of the electrodes had to be carefully excluded.

As negative electrodes we used pure zinc amalgam (1 part of zinc to 9 parts of mercury) as used in the CLARK standard-cell. The zinc was a very pure specimen from MERCK of Darmstadt in which iron was not even detectable. The mercury was first shaken with nitric acid and then distilled twice in vacuum according to HULETT's<sup>2)</sup> method. As we know, the potential difference between this amalgam and pure zinc is very small. Previous experiments by one of us<sup>3)</sup> have shown that this difference is only 0.00048 volt. at 0° and 0.000570 volt. at 25°.

As positive electrode we used at first a thick wire of pure copper. The copper sulphate solution in the different cells was prepared

<sup>1)</sup> Philosophical magazine (5), **13**, 265 (1882); FLEMING, *ibid.* (5), **20**, 126 (1885).  
 Sr. LINDECK, *Zeitschr. für Instrumentenkunde* **12**, 17 (1892). Comp. also CARHART, *Primary Batteries* (Boston 1899). Literature up to 1893 in: WIEDEMANN, *die Lehre von der Elektrizität*. (Braunschweig 1893), pag. 798.

<sup>2)</sup> *Zeitschr. für phys. Chemie* **33**, 611 (1900).

<sup>3)</sup> COHEN, *Zeitschr. für phys. Chemie* **34**, 619 (1900).

by first making a saturated solution at  $15^{\circ}$ . Pure, MERCK's copper sulphate (free from iron) was dissolved in water and boiled with copper hydroxide to remove traces of free acid. After filtration the liquid was cooled and after introducing a crystal of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  set aside to crystallise. The salt was then shaken for a long time (3 to 5 hours) with water at  $15^{\circ}$  in a thermostat, use being made of NOYES<sup>1)</sup> shaking apparatus. All the thermometers used in this investigation were tested by means of a standard thermometer from the "Physikalisch-technische Reichsanstalt" at Charlottenburg.

To make sure that complete saturation had indeed been attained we took after 3 and 5 hours small samples from the solution in the shaking bottles and analysed these liquid by means of NEUMANN's electrolytic process<sup>2)</sup>.

In this way we found:

(5 hours) 100 parts of water dissolve 19.22 parts of anhydrous  $\text{CuSO}_4$ .

(3 hours) 100 parts of water dissolve 19.28 parts of anhydrous  $\text{CuSO}_4$ .

The zinc sulphate solutions were prepared from a solution which was saturated at  $15^{\circ}$  in the same thermostat as the copper sulphate solutions. The different dilutions were done by weighing.

The zinc sulphate gave no reaction with congo-red; moreover the same preparation had served in the construction of CLARK-cells which appeared to be perfectly correct. By way of a check we also determined the quantity of  $\text{ZnSO}_4$  which at  $15^{\circ}$  is present in the saturated solution. A weighed quantity of the solution was evaporated in a platinum dish and the residue ( $\text{ZnSO}_4 \cdot 1 \text{H}_2\text{O}$ ) was weighed<sup>3)</sup>. In 100 grams of water we found 50.94 grams of  $\text{ZnSO}_4$  (as anhydride) whereas previous determinations had given 50.88. If we accept the figure 50.94, the saturated solution then contains at  $15^{\circ}$ , 150.56 grams of  $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$  to 100 grams of water. We fail to see how CHAUDIER has arrived at the figure 200 (see table 1).

6. Measurements with DANIELL-cells are rather difficult, for if the smallest amount of copper sulphate solution comes in contact with

1) Zeitschr. für phys. Chemie 9, 603 (1892).

2) NEUMANN, Analytische Elektrolyse der Metalle, (Halle 1897). Pag. 106.

We may casually remark that the figures given in the literature for the solubility of copper sulphate are incorrect. Compare: ERNST COHEN, Vorträge für Aerzte über physikalische Chemie (Leipzig 1901) pag. 70.

3) See CALLENDAR en BARNES, Proc. Royal Society 62, 147 (1897); ERNST COHEN, Zeitschrift für phys. Chemie 34, 181 (1900).

the zinc electrode by diffusion, the E. M. F. of the system is diminished considerably.

FLEMING for instance states, "the smallest deposit of copper upon the zinc, due to diffusion of the coppersalt into the zinc is indicated by a marked depression amounting to 2 or 3 percent", whilst WRIGHT (after prolonged diffusion) noticed depressions up to 6 percent.

After a few preliminary experiments which convinced us of the accuracy of these remarks we constructed for the definitive measurements the little apparatus shown in fig. 1.

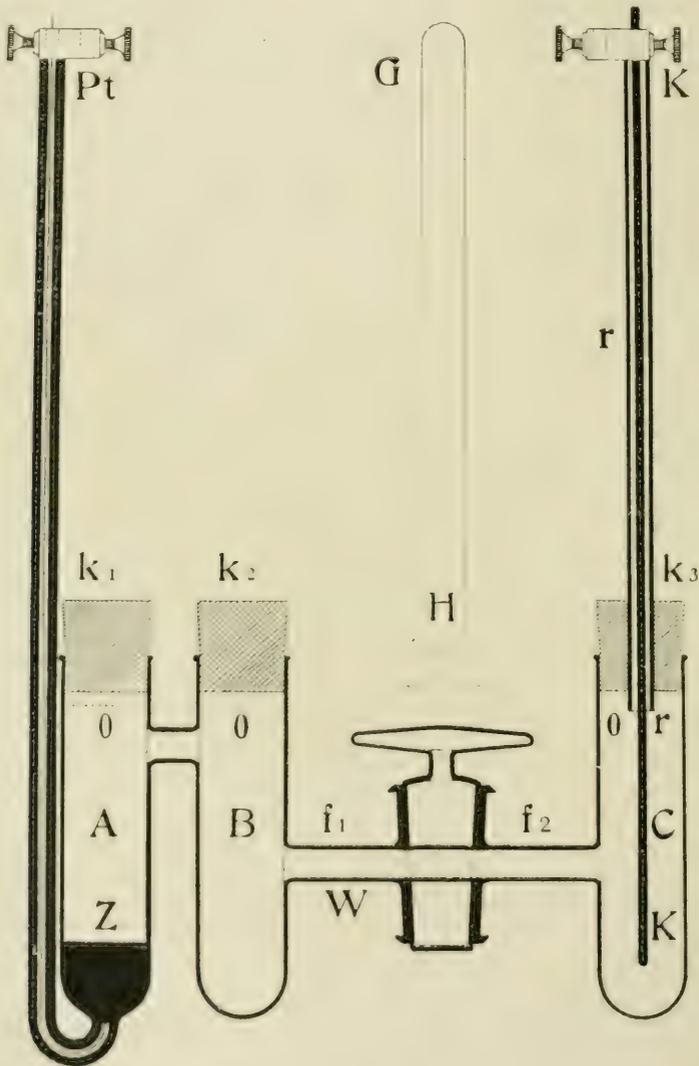


Fig. 1.

It consists of three tubes  $A$ ,  $B$ ,  $C$ , (8 cm. high, internal diameter 1.8 cm.) which communicate by means of connecting tubes. To the tube  $f_1, f_2$  a glass tap with a very wide bore (5 or 6 m.m.) is attached. The zinc amalgam is introduced into  $A$  and the platinum wire  $Pt$  is then fused into it.  $A$  and  $B$  also  $f_1$  are now filled with the zinc sulphate solution after the bore of the tap has been plugged with fat-free cottonwool previously sucked in the same zinc sulphate solution. While the tap is still closed, the saturated copper sulphate solution is poured into  $C$  and also into  $f_2$ : The cell is now closed with the india-rubber corks  $K_1$ ,  $K_2$  and  $K_3$ . Through  $K_3$  is introduced a thin glass tube reaching just below the cork. Through this tube the copper electrode  $K$  may be introduced into the solution when the measurements take place. The whole apparatus is now plunged as deep as possible in a thermostat ( $15^\circ$ ). If required the tap may be opened or closed by means of the wooden rod  $GH$ .

By the introduction of the tube  $B$  the possibility of contact of the zinc electrode with the copper sulphate solution is quite excluded. Even if a trace of copper sulphate has diffused into the lower part of  $B$  (if the copper solution is lighter than the zinc solution, the former will float in  $B$  on the latter) we never find a trace of copper in the tube  $A$ . In the final experiments, the measurements lasted so short a time that as a rule no copper diffused even into  $B$ .

7. After preliminary experiments had shown that the cells cannot be reproduced when we make use of copper electrodes which have been cleared with nitric acid, we afterwards followed the direction of WRIGHT and FLEMING who electrolytically cover the copper electrode with a layer of copper immediately before the measurement. For this purpose we used the bath described by OETTEL<sup>1)</sup> for the copper coulometer. After being copperplated the electrode was rinsed with distilled water and dried with cottonwool. It was then at once put through the tube into the cell. We always take care that only the electrolytically copper plated part of the electrode gets into contact with the liquid.

8. The E. M. F. of the cells was determined by the compensation method of POGGENDORFF. As working cell we used a storage

<sup>1)</sup> Electrochemische Uebungsaufgaben (Halle 1897) pag. 5. All copper electrodes were always copperplated during 10 minutes with the same current-strength (0.15 ampère) (or density) and at the same temperature. We have also tried, but unsuccessfully, to work with copper amalgam. As to copper amalgam, compare PETTENKOFER, DINGLER Polytechnisches Journal **109**, 444 (1848) and v. GERSHEIM. Ibid. **147**, 462 (1858).

cell (Deutsches Telegraphenelement), as normal cell a WESTON-cell which was always kept in a thermostat at  $25^{\circ}$ .

In this thermostat was also placed a CLARK normal cell to allow comparison between the normal elements.

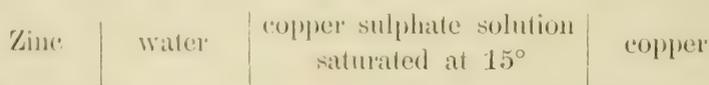
The rheostats used (2 rheostats of 11111.11 ohms each HARTMANN and BRAUN) were carefully compared with a third rheostat standardised by the "Physikalisch-Technische Reichsanstalt."

9. The measurements took place as follows: after a cell had been filled with the required solutions it was (without the copper electrode) placed in the thermostat at  $15^{\circ}$ . After having reached that temperature the copper electrode was taken from the copperplating bath and after having been treated as directed it was introduced through the tube into the solution. The tap was now opened and the measurement carried out; this lasted 1 or 2 minutes. When the tap had been closed, the cell was taken from the thermostat. The solution in A was then tested for copper, but as already stated not the slightest trace of copper was found in this part of the apparatus.

10. As the measurements of ALDER WRIGHT, FLEMING and LORD RAYLEIGH<sup>1)</sup>, which were done with fairly concentrated solutions of zinc sulphate had proved that the reproduction of these cells to less than 1 millivolt is almost impossible and as our own experiences had shown us that with more dilute zinc sulphate solutions we get still greater deviations, we only give our measurements in millivolts although the method of measuring employed rendered the determination of tenths of millivolts (and less) quite possible.

As CHAUDIER only gives one series of measurements we can say nothing as to the reproduceableness of his cells. According to our experience no importance need be attached to statements of tenths of millivolts. Whether it would be possible to attain a greater accuracy when working with solutions quite free from air is a matter which we cannot go into any further as our results are quite accurate enough to completely answer the question in dispute<sup>2)</sup>.

11. Before proceeding to communicate our figures we would point out that a cell constructed according to the scheme:



cannot practically be classed among the reversible cells.

<sup>1)</sup> Transactions of the Royal Society of London. Vol. 76, 800 (1886).

<sup>2)</sup> See EBELING, WIED. Annalen, 30, 530 (1887) and G. MEYER, *ibid*, 33, 265 (1888).

We have, therefore, not repeated CHAUDIER's experiment with this cell. When we consider that cells with very dilute solutions show deviations amounting to 6 millivolt, we cannot expect much from measurements with an element of the kind described.

12. The subjoined table contains the results of our measurements. Below I and II are placed the values of the E. M. F. which we found for the same cell in independent experiments. From these figures it may at the same time be seen in how far the said cells may be reproduced.

TABLE II.

Grams of $ZnSO_4 \cdot 7H_2O$ to 100 gram water.	Electromotive force at 15° 0 C. in Volt. (COMMELIN and COHEN).			Electromotive force at 15° 0 in Volt. (CHAUDIER).
	I	II	average.	
$\frac{1}{12}$	1.443	1.449	1.446	1.4138
$\frac{1}{8}$	1.441	1.446	1.444	1.4151
$\frac{1}{2}$	1.435	1.434	1.435	1.4368
1	1.431	1.431	1.431	1.4331
2	1.425	1.424	1.425	1.4263
4	1.419	1.419	1.419	1.4249
6	1.416	1.416	1.416	1.4208
10	1.412	1.412	1.412	1.4188
30	1.404	1.404	1.404	1.4054
150.65 (saturated).	1.081	1.081	1.081	1.0902 (200 saturated?)

15. From this table it will be seen at once that a maximum value of the E. M. F. at about  $\frac{1}{2}$  gram of  $ZnSO_4 \cdot 7H_2O$  to 100 grams of water, as CHAUDIER claims to have found, does not exist. The progressive change of the values is on the contrary, quite in harmony with the equation given by NERNST, which shows a decrease of the E. M. F. for an increase of the concentration of the zinc sulphate. It would be superfluous to criticise the other conclusions of CHAUDIER as these are based on the figures discussed.

*Utrecht, April 1903.*

**Mathematics.** — “On complexes of rays in relation to a rational skew curve.” By Prof. J. DE VRIES.

(Communicated in the meeting of April 24, 1903).

1. Supposing the tangents of a rational skew curve  $R^n$  of degree  $n$  to be arranged in groups of an involution  $I^p$  of degree  $p$ , let us consider the complex of rays formed by the common transversals of each pair of tangents belonging to a group. So this complex contains each linear congruence the directrices of which belong to a group of  $I^p$ . If these directrices coincide to a double ray  $a$  of  $I^p$  the congruence evidently degenerates into two systems of rays, viz. the sheaf of rays with the point of contact  $A$  of  $a$  as vertex and the field of rays in the corresponding osculating plane  $a$ .

To find the degree of the complex let us consider the involution  $I^p$  of the intersections of the tangents with an arbitrary plane  $\mathfrak{g}$ . The surface of the tangents intersects  $\mathfrak{g}$  according to a curve  $C^m$  of degree  $m = 2(n-1)$  and the complex curve of  $\mathfrak{g}$  envelopes the lines connecting the pairs  $PP'$  of  $I^p$ . This involution having  $(m-1)(p-1)$  pairs in common with the involution forming the intersection with an arbitrary pencil of rays, *the complex is of degree*  $(2n-3)(p-1)$ .

2. We then consider the correspondence between two points  $Q, Q'$  of  $C^m$  situated on a right line  $PP'$ . As  $Q$  lies on the lines connecting any of  $(m-2)(p-1)$  pairs, there are  $(m-2)(p-1)(m-3)$  points  $Q'$ . The correspondence  $(Q, Q')$  has  $(m-2)(m-3)(p-1)^2$  pairs in common with  $I^p$ , so the *complexcurve* has

$$\frac{1}{2}(m-2)(m-3)(p-1)^2 = (n-2)(2n-5)(p-1)^2$$

*double tangents*, the *complexcone* as many *double edges*.

Evidently these double rays form a *congruence* comprised in the complex, of which *order and class are equal to*  $(n-2)(2n-5)(p-1)^2$ .

The *complexcurve* also possesses a number of threefold tangents, each containing three points of  $I^p$  belonging to one and the same group. To find this number we make each point of intersection  $S$  of  $C^m$  with the right line  $PP'$  to correspond to each point  $P''$  of the group indicated by  $P$ . To each point  $P''$  belong  $\frac{1}{2}(p-1)(p-2)$  pairs  $P, P'$ , so  $\frac{1}{2}(p-1)(p-2)(m-2)$  points  $S$ ; each point  $S$  lies on  $(m-2)(p-1)$  connecting lines  $PP'$ , and therefore it is conjugate to  $(m-2)(p-1)(p-2)$  points  $P''$ . Every time  $P''$  coincides with  $S$ , three points  $P$  lie in a right line and each of those points is a coincidence of the correspondence  $(P'', S)$ ; so we find  $\frac{1}{2}(m-2)(p-1)(p-2)$  *threefold tangents*. From this appears at the same time that the

right lines of which each cuts three tangents of  $R^n$  belonging to a same group of  $I^p$ , form a congruence of which order and class are equal to  $(n-2)(p-1)(p-2)$ .

3. Let us consider more closely the group where  $a$  is a double element and  $a'$  one of the other elements. To the just-mentioned congruence evidently belongs the pencil of rays in the plane  $(A, a') \equiv \alpha_1$ , with vertex  $A$  and the pencil of rays in the osculating plane  $\alpha$  with vertex  $(a, \alpha_1) \equiv A_1$ . So the congruence contains at the least  $4(p-1)(p-2)$  pencils of rays; each of the  $2(p-1)$  singular points  $A$  is the vertex of  $(p-2)$  pencils placed in different planes; each of the  $2(p-1)$  singular planes  $\alpha$  bears  $(p-2)$  pencils with different vertices; on the other hand the  $2(p-1)(p-2)$  singular points  $A_1$  and the  $2(p-1)(p-2)$  singular planes  $\alpha_1$  each bear a pencil.

The complex curve is as appears from the above of genus  $\frac{1}{2}[(2n-3)(p-1)-1][(2n-3)(p-1)-2] - (n-2)(2n-5)(p-1)^2 - 3(n-2)(p-1)(p-2)$ . For  $p=3$  this becomes equal to zero which could be foreseen; for, to each point  $P$  of the curve  $C^m$  the connecting line  $P'P''$  can be made to correspond, by which the tangents of the complexcurve coincide one by one with the points of a rational curve.

In a plane  $\varphi$  through a tangent  $a'$  the complexcurve degenerates, a pencil of rays the vertex of which lies on the tangent  $a$  separating itself from the whole.

In a plane  $\alpha$  evidently  $(p-2)$  pencils of rays separate themselves.

4. We shall consider more closely the simplest case, where the complex is determined by a quadratic involution of the tangents of a skew cubic;  $n=3, p=2$ .

If  $A$  and  $B$  are the points of contact of the tangents  $a$  and  $b$  forming the double rays of the involution, and if  $\alpha$  and  $\beta$  are the corresponding osculating planes, we assume as planes of coordinates  $x_1=0, x_2=0, x_3=0, x_4=0$  successively the osculating plane  $\alpha$ , the tangent plane  $(a, B)$ , the tangent plane  $(b, A)$ , the osculating plane  $\beta$ . The curve  $R^3$  is then represented by

$$x_1 : x_2 : x_3 : x_4 = t^3 : t^2 : t : 1,$$

and for its tangents we have the relation

$$P_{12} : P_{13} : P_{14} : P_{23} : P_{24} : P_{34} = t^4 : 2t^3 : 3t^2 : 1 : -2t : t^2.$$

The points  $A$  and  $B$  being indicated by the parameters  $t=0$  and  $t=\infty$ , the parameters  $t$  and  $t'$  of the points of contact of two conjugate tangents satisfy the relation  $t + t' = 0$ .

The coordinates of a common transversal of the tangents ( $t$ ) and ( $-t$ ) evidently satisfy the conditions

$$\left. \begin{aligned} p_{12} - 2tp_{13} + t^2p_{14} + 3t^2p_{23} + t^4p_{34} + 2t^3p_{42} &= 0, \\ p_{12} + 2tp_{13} + t^2p_{14} + 3t^2p_{23} + t^4p_{34} - 2t^3p_{42} &= 0, \end{aligned} \right\}$$

therefore also

$$p_{12} + t^2(p_{14} + 3p_{23}) + t^4p_{34} = 0 \quad \text{and} \quad t^2p_{42} = p_{13}.$$

By eliminating  $t$  we find the equation of the indicated complex:

$$p_{12}p_{42}^2 + p_{13}p_{42}(p_{14} + 3p_{23}) + p_{34}p_{13}^2 = 0.$$

To this *cubic complex* belongs the linear congruence  $p_{13} = 0$ ,  $p_{42} = 0$ . Its directrices  $l$  and  $m$  are represented by  $x_1 = 0$ ,  $x_3 = 0$  and  $x_4 = 0$ ,  $x_2 = 0$ ; the former connects  $A$  with the point  $(a, b)$ , the latter unites  $B$  and  $(\beta, a)$ .

Each ray of the congruence rests on two pairs of tangents; the corresponding parameters are determined by the equation

$$p_{34}t^4 + (p_{14} + 3p_{23})t^2 + p_{12} = 0.$$

So the complexcone has a double edge, the complexcurve a double tangent.

5. This is also evident in the following way. With given values of  $y_1, y_2, y_3, y_4$  the equation  $p_{12} = \lambda p_{13}$  or  $y_2x_4 - y_1x_2 = \lambda(y_3x_1 - y_1x_3)$  represents a plane intersecting the complexcone twice according to  $p_{12} = 0$ ,  $p_{13} = 0$ , and moreover according to a right line of the plane

$$\lambda^2(y_2x_1 - y_1x_2) + \lambda[(y_4x_1 - y_1x_4) + 3(y_3x_2 - y_2x_3)] + (y_4x_3 - y_3x_4) = 0.$$

So  $p_{13} = 0$ ,  $p_{12} = 0$  is a double edge.

If the plane  $y_2x_4 - y_1x_2 = \lambda(y_3x_1 - y_1x_3)$  is to touch the complexcone along the double edge, the three planes

$$y_3x_1 - y_1x_3 = 0 \quad , \quad y_1x_2 - y_2x_4 = 0,$$

$$(\lambda^2y_2 + \lambda y_4)x_1 + (3\lambda y_3 - \lambda^2y_1)x_2 + (y_4 - 3\lambda y_2)x_3 - (\lambda y_1 + y_3)x_4 = 0$$

must pass through *one* right line, so

$$\left. \begin{aligned} \lambda^2y_2 + \lambda y_4 &= \varrho y_3 \quad , \quad 3\lambda y_3 - \lambda^2y_1 = \sigma y_4, \\ y_4 - 3\lambda y_2 &= -\varrho y_1 \quad , \quad \lambda y_1 + y_3 = \sigma y_2. \end{aligned} \right\}$$

must be satisfied.

By eliminating  $\varrho$  or  $\sigma$  we find

$$\lambda^2y_1y_2 + \lambda(y_1y_4 - 3y_2y_3) + y_3y_4 = 0.$$

The roots of this quadratic equation determine the tangent planes of the complexcone along the double edge, which becomes a cuspidal edge when

$$4y_1y_2y_3y_4 = (y_1y_4 - 3y_2y_3)^2,$$

that is when

$$y_2y_4 = y_3y_3 \quad \text{or} \quad y_1y_4 = 9y_2y_3.$$

So these quadratic skew surfaces of which the first evidently passes through  $R^3$  contain the vertices of the *complexcones having a cuspidal edge*.

6. For the points  $P$  of the  $R^3$  this cone of course degenerates into the plane connecting  $P$  with the tangent  $\rho'$  in the conjugate point  $P'$  and a quadratic cone touching that plane.

For points on the right lines  $l$  and  $m$  the complexcone must consist of a plane counted double and the single plane  $x_1=0$  or  $x_2=0$ . For, each ray in  $\alpha$  and  $\beta$  belongs to the complex, whilst all right lines resting on  $l$  and  $m$  are double rays of the complex. Indeed the substitution  $y_1=0$ ,  $y_3=0$  in the equation of the complex gives the relation  $x_1(y_2x_1 - y_4x_2)^2 = 0$ .

For points on one of the tangents  $a$  and  $b$  the complexcone breaks up into the plane  $\alpha$  or  $\beta$  and into a quadratic cone touching it.

For a point of the intersection of  $a$  and  $\beta$  we find a degeneration into three planes.

For the complexcurves analogous considerations hold good; e. g. the complexcurve degenerates into three pencils of rays when the plane passes through  $AB$ .

7. The complexcone degenerates into a plane and a quadratic cone if the vertex lies in  $\alpha$  or in  $\beta$  or on the surface of the tangents of  $R^3$ . In the former case  $\alpha$  or  $\beta$  belong to it; in the latter the plane through the vertex  $P$  and the conjugate tangent  $\rho'$ .

To investigate whether there are more points for which such a degeneration takes place, we suppose that the equation of the intersection of the complexcone with  $x_4=0$ , thus that

$$-y_1y_4x_2^3 + y_1^2x_3^3 - y_3y_4x_1^2x_2 + y_3^2x_1^2x_3 + (y_2y_1 - 3y_3^2)x_2^2x_1 + 3y_1y_3x_2^2x_3 - 2y_1y_3x_3^2x_1 - 3y_1y_2x_3^2x_2 + (y_1y_1 + 3y_2y_3)x_1x_2x_3 = 0,$$

is deducible to the form

$$(b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + 2b_{12}x_1x_2 + 2b_{13}x_1x_3 + 2b_{23}x_2x_3)(c_1x_1 + c_2x_2 + c_3x_3) = 0.$$

Then the following conditions are to be satisfied:

$$\begin{aligned} b_{11}c_1 &= 0, & b_{22}c_2 &= -y_1y_4, & b_{33}c_3 &= y_1^2, \\ b_{11}c_2 + 2b_{12}c_1 &= -y_3y_4, & b_{11}c_3 + 2b_{13}c_1 &= y_3^2, & b_{22}c_1 + 2b_{12}c_2 &= y_2y_4 - 3y_3^2, \\ b_{22}c_3 + 2b_{23}c_2 &= 3y_1y_3, & b_{33}c_1 + 2b_{13}c_3 &= -2y_1y_3, & b_{33}c_2 + 2b_{23}c_3 &= -3y_1y_2, \\ & & 2(b_{12}c_3 + b_{23}c_1 + b_{13}c_2) &= y_1y_4 + 3y_2y_3. \end{aligned}$$

Let us in the first place put  $b_{11}=0$  and  $c_1=y_3$ , then  $2b_{12}$  is equal to  $-y_4$  and  $2b_{13}$  equal to  $y_3$ . Further we find  $b_{33}=-y_1$  and  $c_3=-y_1$ . After some deduction we get as only condition

$$y_1^2 y_4^2 + 4y_1 y_3^2 - 6y_1 y_2 y_3 y_4 - 3y_2^2 y_3^2 + 4y_2^3 y_4 = 0,$$

or

$$(y_1 y_4 - y_2 y_3)^2 = 4(y_1 y_3 - y_2^2)(y_2 y_4 - y_3^2),$$

that is *the vertex of the complex cone belongs to the surface of tangents.*

If we put  $c_1 = 0$ , we then arrive after excluding  $y_1 = 0$  and  $y_4 = 0$  (for which the indicated degeneration always takes place) at the double condition

$$y_2 y_4 = y_3^2 \text{ and } y_1 y_4 = y_2 y_3,$$

that is at the points of  $R^3$ .

8. Let us suppose that the tangents of  $R^3$  are arranged in the triplets of a  $J^3$ . To determine the degree of the complex of the common transversals of the pairs of tangents we can also set about as follows. In an arbitrary pencil we consider the correspondence of two rays  $s$  and  $s'$ , which are cut by two tangents belonging to  $J^3$ . To the coincidences of this correspondence (8, 8) belong the four rays resting on the double rays  $a, b, c, d$  of  $J^3$ ; the others are united in pairs to six rays, each resting on two tangents of a triplet, *so the complex is of degree 6.*

To find the degree of the congruence of the right lines, each resting on the three tangents of a group, let us consider the rays they have in common with the analogous congruence belonging to a second  $J^3$ . If  $r_1, r_2$  is one of the four common pairs of the two involutions, and  $r_3$  and  $r_3'$  successively the tangent forming with  $r_1$  and  $r_2$  a group, the common transversals of  $r_1, r_2, r_3$  and  $r_3'$  belong to the two congruences<sup>1)</sup>. Evidently they can have no other rays in common than those eight, which are indicated by these; consequently the congruence is of order two.

The complex cone of an arbitrary point  $P$  has as appears from the above, *two threefold edges*; as it has to be rational, it has moreover *four double edges.*

If  $P$  lies on the surface of tangents of  $R^3$ , this cone degenerates into the system of planes which connect  $P$  with the two tangents conjugate to  $p$  and a biquadratic cone with threefold edge.

9. The quadratic scrolls determined by the triplets of tangents, evidently form a system of surfaces two of which pass through any point and two of which touch any plane. This system is thus represented in point- or tangential coordinates by an equation of the form

<sup>1)</sup> This consideration leads to no result if we consider a rational skew curve of higher order.

$$P + 2\lambda Q + \lambda^2 R = 0.$$

From this ensues that all the surfaces of this system have the eight common points (tangential planes) of  $P=0$ ,  $Q=0$ ,  $R=0$  in common.

The degenerations of this system are four figures consisting each of two planes as locus of points and of two points as locus of tangential planes. One of those figures is formed by the planes  $\alpha$  and  $\alpha_1 \equiv (Aa')$  and the points  $A$  and  $A_1 \equiv (aa')$ .

The eight common points  $A_2, B_2, C_2, D_2, A_3, B_3, C_3, D_3$  and the eight common tangential planes  $\alpha_2, \beta_2, \gamma_2, \delta_2, \alpha_3, \beta_3, \gamma_3, \delta_3$  of the scrolls are *singular* for the congruence (2,2). The remaining singular points and planes are evidently  $A, B, C, D, A_1, B_1, C_1, D_1$  and  $\alpha, \beta, \gamma, \delta, \alpha_1, \beta_1, \gamma_1, \delta_1$ . These 16 points and 16 planes form the well known configuration of KUMMER.

We can choose the notation in such a way, that  $A_2$  bears the planes  $\beta, \gamma, \delta, \alpha_1$  and  $A_3$  the planes  $\beta_1, \gamma_1, \delta_1, \alpha$ , etc. Let us bear in mind that three osculating planes of  $R^3$  intersect each other in a point of the plane of their points of contact and let us further mark the symmetry of the figure, we can then easily deduce from the preceding, that

in $\alpha$	the points	$A, A_1, A_3, B_2, C_2, D_2,$
" $\alpha_1$	" "	$A, A_1, A_2, B_3, C_3, D_3,$
" $\alpha_2$	" "	$A_1, A_2, A_3, B, C, D,$
" $\alpha_3$	" "	$A, A_2, A_3, B_1, C_1, D_1,$

are situated, whilst

$A$	bears the planes	$\alpha, \alpha_1, \alpha_3, \beta_2, \gamma_2, \delta_2,$
$A_1$	" "	$\alpha, \alpha_1, \alpha_2, \beta_3, \gamma_3, \delta_3,$
$A_2$	" "	$\alpha_1, \alpha_2, \alpha_3, \beta, \gamma, \delta,$
$A_3$	" "	$\alpha, \alpha_2, \alpha_3, \beta_1, \gamma_1, \delta_1.$

It is clear that for each of these 16 points the complexcone is composed of a plane counted double and a cone of degree four.

**Mathematics.** — “*The singularities of the focal curve of a curve in space.*” By DR. W. A. VERSLUYS. (Communicated by Prof. P. H. SCHOUTE.)

In paper N<sup>o</sup>. 5 of the “K. A. v. W.” at Amsterdam, Vol. XIII, I have deduced some formulae expressing the singularities of the focal developable and of the focal curve in function of the singularities of a plane curve.

In like manner it is possible to deduce the following formulae which express the singularities of the focal developable and of the

focal curve of a curve in space in function of the singularities of this curve.

Let the curve be of degree  $\mu$ , of rank  $\varrho$ , of class  $\nu$ ; let its number of stationary points be  $z$ , that of its stationary tangents  $\theta$ . Suppose the curve to have no real nodes or double tangents and no particular position with respect to the plane at infinity or with respect to the imaginary circle at infinity.

In that case the singularities of the evolute or of the cuspidal curve of its focal developable (G. DARBOUX: Classe Remarquable etc. p. 19) are the following:

rank,  $r = 2(\mu + \varrho)$ .

class,  $m = 2\varrho$ .

number of stationary planes,  $\alpha = 2(\nu + \theta)$ .

double osculating planes,  $G = \varrho^2 - \varrho - \mu - 3(\nu + \theta)$ .

stationary tangents,  $v = 0$ .

nodes,  $H = z = 3(\mu - \varrho) + \nu + \theta$ .

double tangents,  $\omega = 0$ .

degree,  $n = 2(3\mu + \nu + \theta)$ .

degree nodal curve;  $x = 2(\mu + \varrho)^2 - 10\mu - 2\varrho - 3(\nu + \theta)$ .

number of planes through two lines which pass through a given point,  $y = 2(\mu + \varrho)^2 - 4\mu - 4\varrho - (\nu + \theta)$ .

stationary points,  $\beta = 12\mu - 4\varrho - 6(\nu + \theta)$ .

The chief singularities of the focal curve are:

degree,  $n = 2\mu^2 + 4\mu\varrho + \varrho^2 - 11\mu - \varrho - 3(\nu + \theta)$ .

rank,  $r = 4\mu\varrho + \varrho^2 - 4\mu - 4\varrho$ .

number of stationary tangents,  $v = 0$ .

class,  $m = (3\mu + 2\nu + 2\theta)(2\mu + \varrho) + 3\mu\varrho - 36\mu + 12\varrho - (\nu + \theta)$ .

number of stationary points,  $\beta = 2(3\mu + \nu + \theta)(2\mu + \varrho) - 57\mu + 21\varrho - 27(\nu + \theta)$ .

" " planes,  $\alpha = 6(2\mu + \nu + \theta)(2\mu + \varrho) - 4\mu^2 - 2\mu\varrho - 2\varrho^2 - 107\mu + 47\varrho - 57(\nu + \theta)$ .

When comparing these singularities with the values of the singularities of the evolute and of the focal curve of a plane curve, we see that they differ only in the rank of the curve in space being substituted for the class of the plane curve and in the number of stationary tangents  $\iota$  being replaced by  $(\nu + \theta)$ . From this follows that the singularities of the evolute and of the focal curve of a curve in space  $c$  are the same as those of a plane curve  $d$ , which is the projection of  $c$  on an arbitrary plane from an arbitrary point.

**Physics.** — “On the double refraction in a magnetic field near the components of a quadruplet.” By Prof. P. ZEEMAN and J. GEEST.

On a former occasion the results were communicated to the Academy, of an investigation on the magnetic rotation of the plane of polarization in sodium vapour, in the immediate neighbourhood of the absorption lines.<sup>1)</sup>

In the case of very thin vapours this rotation appeared to be positive outside the components of the doublet, in which the original spectral line is resolved by the influence of the magnetic forces; between the components, however, it becomes negative and very large. In these experiments the light of course passed through the vapour in the direction of the lines of force.

In the same way, if the light is transmitted through sodium vapour in a direction normal to the lines of force, we may expect from the examination of the immediate neighbourhood of the components, in which the spectral line is split up by the magnetic forces, results which are of theoretical importance.

VOIGT has deduced from his theory of magneto-optical phenomena the existence of a double refraction, which must be produced in isotropic media, as soon as they are placed in a magnetic field, but which should only be observable in the neighbourhood of an absorption line.<sup>2)</sup> VOIGT, together with WIECHERT, has observed, that plane polarised light of a period near that of the lines  $D_1$  and  $D_2$ , is no longer plane polarised but has become elliptically polarised when it has traversed the flame, there being generated a difference of phase between the components vibrating parallel and those vibrating perpendicularly to the field.

This elliptical polarisation was demonstrated by the above mentioned physicians with the aid of a BABINET compensator, using a flame with *much* sodium and a small ROWLAND grating.

The object of our investigation of the magnetic double refraction was to examine the phenomena, which show themselves, if, beginning with very small vapour densities, the quantity of sodium is gradually increased. The present communication deals only with the line  $D_1$  in the case of very small densities. This line is resolved into a quadruplet by the action of the magnetic field.

The grating employed for this investigation and its mounting for

<sup>1)</sup> ZEEMAN. Proc. Roy. Acad. Amsterdam Vol. V p. 41, 1902, cf. also HALLO Dissertatie. Amsterdam, 1902.

<sup>2)</sup> VOIGT. Göttinger Nachrichten. Heft 4. 1898; WIEDEMANN'S *Annalen*. Bd. 67. p. 359, 1899.

parallel light (which was necessary also now) have been described already more than once.<sup>1)</sup>

The light from an arc-lamp or from the sun passed successively through a Nicol's prism, whose plane of vibration was inclined at an angle of  $45^\circ$  to the horizon, the magnetic field with its lines of force normal to the beam, a second Nicol at right angles to the first. Between the Nicols the BABINET compensator was placed, the edges of the two prisms being horizontal. An image of the compensator was formed on the slit of the spectral apparatus; in the middle of this image the central dark interference fringe, surrounded by the coloured ones, was seen. In the spectrum a pair of dark interference fringes are observed and with the field off, only the fine absorption lines of the vapour are seen. Generally the reversed sodiumline is observed already in the spectrum of the arc-light itself and then the presence of sodium vapour between the poles makes of course no difference at all. In order to obtain the degree of sharpness of the interference fringes, necessary for this part of the investigation, we tried several compensators. Sufficient results were obtained with a BABINET compensator of which the prisms had angles of about  $50'$ , obtained from the firm STEEG & REUTER.

The light passed the flame (a gas flame fed with oxygen) over a length of nearly  $1\frac{1}{2}$  cm. If the field had an intensity of about 23000 C. G. S. units, the quantity of sodium in the flame being very



small, the image observed was very similar to that represented in Fig. 1. The latter is constructed with the aid of photographic negatives and of eye observations. The whole phenomenon is of course very delicate as it only extends to the region of the magnetically broadened  $D_1$  line; moreover it depends very much on the quantity of sodium present. We did not yet succeed in getting negatives, which showed the parts which are of very unequal intensity all equally well.

Fig. 1. Already some time ago Prof. VOIGT was so kind to inform one of us of the result, which according to his theory may be anticipated in the case of a quadruplet.

This conclusion is easily arrived at, if the calculation be simplified by applying a certain approximation, the soundness of which cannot be judged a priori, because constants appear whose numerical value is not yet known. With this reservation the behaviour predicted

<sup>1)</sup> ZEEMAN l.c. and Arch. Néerl. (2) 5. 237. 1900.

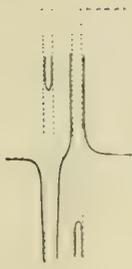


Fig. 2.

by theory is represented in Fig. 2. The dotted vertical lines are the four components of the quadruplet.

In comparing the figures 1 and 2 one must take into consideration, that in Fig. 2 is represented the shape of the fringes, which arise from a single horizontal band. In Fig. 1 in the central part of the field also occur parts, originating from fringes lying above and under the middle. The vertical medium line of Fig. 1 corresponds to the almost ever present absorption line due to the arc light and is thus in no way connected with the phenomenon which occupies us.

The agreement in the region between the two interior components of the quadruplet is undoubtedly of great importance. The whole form of the double curved line may certainly be regarded as a confirmation of theory. How far the darker parts between the exterior components in the middle of Fig. 1 correspond to the U-shaped parts of Fig. 2 is at present not yet to be decided.

**Chemistry.** — “*The course of the melting-point-line of alloys.*” (Third communication). By J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

I. I have shown in two papers (these proceedings Jan. 31 and March 28, 1903) that the expression (see the second paper):

$$T = T_0 \frac{1 + \frac{ax^2}{(1+rx)^2}}{1 - \theta \log(1-x)}, \dots \dots \dots (1)$$

very accurately represents the solidification temperatures of *tin-amalgams*. This equation may be derived from the general expressions for the molecular thermodynamic potentials of one of the two components in solid condition and in the fluid alloy.

I also pointed out (in the first paper), that already the simple formula

$$T = \frac{T_0}{1 - \theta \log(1-x)} \dots \dots \dots (2)$$

*qualitatively* represents the course of the melting-point-line perfectly. This is simply done by not omitting the logarithmic function  $\log(1-x)$ . Though it is a matter of course, that  $-\log(1-x)$  can only be replaced by  $x$ , or  $x + \frac{1}{2}x^2 +$  etc. in the case that  $x$  is very small, it

seems necessary to continually draw attention to this circumstance. Already in 1893 in his thesis for a doctor's degree: "De afwijkingen van de wetten voor verdunde oplossingen" HONDIUS BOLDINGH used the function  $-\log(1-x)$ ; also the correction term  $rx^2$ , omitting however the denominator  $(1+rv)^2$ . LE CHATELIER<sup>1)</sup> used the simple equation (2) in a somewhat modified form for the melting-point-curves of alloys. The way however in which he derived this equation is totally wrong<sup>2)</sup>.

II. Many melting-point-curves show the same type as those of tin-amalgams; it may therefore be important to investigate, whether they also may be represented by formula (1). It must however be observed, that this formula is applicable only in the case that the *solid phase does not form any mixed crystals*. If the formula (1) does not hold good, this may therefore indicate the occurrence of mixed crystals in the solid phase, though it is of course also possible that other influences e. g. dissociating multiple molecules have caused the deviation.

In 1897 HEYCOCK and NEVILLE i. a. made experiments on a great many alloys<sup>3)</sup>. They found that the alloy *silver-lead* shows the type of tin-mercury very accurately (comp. the figure on p. 59 of their paper). I have subjected the data relating to this point (comp. the tables of p. 37 and 39) to some numerical investigations.

The initial course is again nearly straight — up to about 20 atom percents of lead — and this part yields for  $\theta$  the value 0,805. If we now use this value for the calculation of the quantities  $a$  and  $r$  from the observations at lower temperature, we do not find constant values, as in the case of tin-mercury, but considerably different values according as we have calculated these constants at mean temperatures or at low temperatures. If we take the data for  $x=0,63$  and  $x=0,80$ , or  $x=0,63$  and  $x=0,96$  (the eutectic point) as basis for our calculation, then we find in both cases:

$$a = 0,355 \quad ; \quad r = -0,325.$$

The following table may show how bad the agreement is, specially for the mean temperatures:

<sup>1)</sup> See i. a. "Rapport etc." (Paris, Gauthiers-Villars): La constitution des alliages métalliques par S. W. ROBERTS-AUSTEN et A. STANSFIELD. (1900), p. 24.

<sup>2)</sup> On different occasions I have pleaded already before for not omitting the function  $\log(1-x)$ . (comp. i. a. Zeitschr. für Phys. Ch. **15**, p. 457 sequ. 1894).

<sup>3)</sup> Complete Freezing-Point Curves of Binary Alloys, containing Silver or Copper together with another metal (Phil. Trans. of the R. S. of London, Series A, Vol. 189 (1897), p. 25--69).

## SILVER-LEAD. 1)

$x$	$x^2$	Denominator $1 - 9 \log(1-x)$	$zx^2$	$(1+x)^2$	Numerator $\frac{ax^2}{(1+rx)^2}$	$r - \frac{27x^2}{2}$ calculated	id. found	$\Delta$
0	0	1.0000	0	1.0000	1.0000	959.1	959.1	0
0.0052	0.00003	1.0042	0.00001	0.9966	1.00001	954.0	954.3	- 0.3
0.0103	0.00011	1.0083	0.00004	0.9934	1.00004	948.9	949.0	- 0.1
0.0154	0.00024	1.0125	0.00008	0.9900	1.00009	944.0	944.0	0
0.0254	0.00065	1.0207	0.00023	0.9835	1.0002	934.5	934.4	+ 0.1
0.0361	0.00130	1.0296	0.00046	0.9767	1.0005	924.3	924.4	- 0.1
0.0504	0.00254	1.0416	0.00090	0.9675	1.0009	910.9	910.4	+ 0.5
0.0733	0.00537	1.0613	0.00191	0.9530	1.0020	890.3	886.6	+ 3.7
0.1057	0.01117	1.0900	0.00397	0.9324	1.0043	862.1	853.4	+ 8.7
0.1360	0.01850	1.1177	0.00657	0.9136	1.0072	837.2	820.0	+17.2
0.1732	0.03000	1.1531	0.01065	0.8906	1.0120	808.4	782.7	+25.7
0.2156	0.04648	1.1955	0.01650	0.8647	1.0191	777.2	741.6	+35.6
0.2537	0.06436	1.2356	0.02285	0.8418	1.0271	751.1	710.0	+41.1
0.2949	0.08697	1.2813	0.03085	0.8176	1.0378	725.0	684.1	+40.9
0.3432	0.1178	1.3385	0.04182	0.7894	1.0530	696.3	659.5	+36.8
0.4038	0.1631	1.4164	0.05791	0.7548	1.0767	663.4	635.4	+28.0
0.4542	0.2063	1.4876	0.07324	0.7266	1.1007	638.5	619.3	+19.2
0.4966	0.2466	1.5527	0.08754	0.7032	1.1244	619.1	606.2	+12.9
0.5330	0.2841	1.6131	0.1019	0.6836	1.1476	603.4	596.1	+ 7.3
0.5851	0.3423	1.7083	0.1215	0.6558	1.1853	581.9	580.8	+ 1.1
*0.6312	0.3984	1.8032	0.1414	0.6319	1.2238	563.1	563.0	+ 0.1*
0.6790	0.4610	1.9149	0.1637	0.6073	1.2696	543.9	548.3	- 4.4
0.7042	0.4959	1.9808	0.1761	0.5946	1.2962	533.2	536.9	- 3.7
0.7353	0.5407	2.0702	0.1920	0.5791	1.3316	519.5	523.6	- 4.1
0.7692	0.5917	2.1816	0.2101	0.4727	1.3735	503.0	505.5	- 2.5
*0.8064	0.6503	2.3221	0.2309	0.5625	1.4241	482.5	481.6	+ 0.9*
0.8333	0.6944	2.4425	0.2465	0.5445	1.4635	465.1	460.6	+ 4.5
*0.9615	0.9245	3.6226	0.3282	0.5318	1.6943	303.2	303.3	- 0.1*

1) The values of  $x$  marked with asterics are those which are used for the calculation of the constants  $z$  and  $r$ .

Between  $x=0,10$  and  $x=0,53$  the agreement is decidedly bad; at lower temperatures slightly better. It is striking that the value we find for  $\alpha$  is much too large, namely 0,355; for tin-mercury we found for  $\alpha$  only the value 0,0453.

We will further investigate whether the value of  $\theta$  which is calculated from the initial straight part of the melting-point-line, namely  $\theta=0,805$ , is in agreement with the latent heat of solidification of pure silver.

As

$$\theta = \frac{RT_0}{q_0},$$

and as PERSON has found  $q_0 = 107,94 \times 21,07 = 2274$  Gr. kal., we should have for  $\theta$ :

$$\theta = \frac{2 \times 1232}{2274} = 1,084.$$

We have, however, found the much *smaller* value 0,805. This indicates the occurrence of mixed crystals already in the initial part of the melting-point curve, unless we assume, either that the value of PERSON is about 1,35 times too small, or that the association of the lead, contained in the silver, is 1,35.

III. Let us discuss in the second place the melting-point curve of *silver-tin*. We conclude at once from the figure of HEYCOCK and NEVILLE, that complications, mixed crystals for instance, must occur. For though the melting-point curve from 30 atom-percents tin upwards shows the normal typical course, the initial part, instead of being nearly straight, is strongly concave towards the side of silver, so that *two* inflection points occur, quite contrary to the course indicated by formula (1) or (2).

It is accordingly impossible to determine the value of  $\theta$  from the initial part of the curve. If we calculate  $\theta$ ,  $\alpha$  and  $r$  from three observations, for instance  $x=0,43$ ,  $x=0,61$  and  $x=0,86$ , then we get with:

$$T_0 = 961,5^1) + 273,2 = 1234,7$$

the following values (comp. the table of HEYCOCK and NEVILLE, p. 40 and 41):

$$\theta = 1,491 \quad ; \quad \alpha = 0,718 \quad ; \quad r = - 0,277.$$

<sup>1)</sup> The value 959°.2 given by HEYCOCK and NEVILLE has been augmented to 961°.5 on account of the accurate observations of HOLBORN and DAY (quoted in Z. f. Ph. Ch. 35, p. 490—491), from which appeared that pure silver, the air being excluded, so that no oxygen can be absorbed, has a higher melting point (961°.5) than silver containing oxygen (955°).

We see that the value calculated for  $\theta$  is considerably higher than the normal value 1,08 and that  $\alpha$  is also again excessively high. In order to get a survey of the *degree* of the deviation from the theoretical course we will perform here the calculation of equation (1) with these values of  $\theta$ ,  $\alpha$  and  $r$ . (see table p. 26).

This bad agreement does not improve considerably if we determine  $\theta$ ,  $\alpha$  and  $r$  from other values of  $x$ , for instance from  $x=0,30$ ,  $x=0,61$  and  $x=0,93$ . For these values of  $x$  we find:

$$\theta = 1,326 \quad ; \quad \alpha = 0,474 \quad ; \quad r = -0,38,$$

so  $\theta$  has come somewhat nearer to 1,08 and  $\alpha$  is also somewhat lower. It is true that the agreement for values of  $x$  below  $x=0,30$  has somewhat though not noticeably improved ( $\Delta = -70,3$  for  $x=0,13$  becomes now  $\Delta = -55,7$ ) but the agreement for values of  $x$  higher than  $x=0,30$  is in general still worse. So we find for instance for  $x=0,47$  for  $\Delta$  the value  $\Delta = +8,5$ , whilst in the above table we found  $\Delta = +2,6$ , etc.

IV. For completeness' sake we shall draw attention to the two very short melting-point curves of lead-silver and tin-silver. We may easily calculate the quantities  $\theta$  from the data of the two eutectic points. As namely these lines may be considered to be straight, we find  $\theta$  immediately from

$$\theta = \frac{T_0 - T}{T \cdot x}.$$

We have for *lead-silver*:

$T_0 = 327,6 + 273,2 = 600,8$  ;  $T = 303,3 + 273,2 = 576,5$  ;  $x = 0,0385 \pm$ ,  
therefore

$$\theta = \frac{24,3}{576,5 \times 0,0385} = 1,095,$$

hence

$$q_0 = \frac{RT_0}{\theta} = \frac{2 \times 600,8}{1,095} = 1097 \text{ Gr. cal.}$$

PERSON found  $q_0 = 5,369 \times 206,9 = 1111$  Gr. cal. The agreement appears to be nearly perfect. From this follows that *silver*, solved in *lead*, occurs in it as *atom*, at least for small concentrations.

As to the melting-point curve *tin-silver* we have for it:

$T_0 = 232,1 + 273,2 = 505,3$  ;  $T = 221,7 + 273,2 = 494,9$  ;  $x = 0,0385 \pm$ .

We find therefore:

$$\theta = \frac{10,4}{494,9 \times 0,0385} = 0,546,$$

and

## SILVER-TIN.

$x$	$x^2$	Denominator $1 - 0.0001(1-x)$	$ax^2$	$(1+ax)^2$	Numerator $\frac{ax^2}{1+(1+ax)^2}$	$T - \frac{27.5}{x^2}$ calculated	id. found	$\Delta$
0	0	1.0000	0	1.0000	1.0000	961.5	959.2	+ 2.3
0.00459	0.0000 <sup>2</sup>	1.0068	0.0000 <sup>2</sup>	0.9975	1.0000 <sup>2</sup>	953.2	956.1	- 2.9
0.01299	0.0001 <sup>7</sup>	1.0195	0.0001 <sup>2</sup>	0.9928	1.0001	938.0	950.0	-12.0
0.03058	0.0009 <sup>4</sup>	1.0463	0.0006 <sup>7</sup>	0.9831	1.0007	907.9	936.3	-28.4
0.04842	0.0023 <sup>4</sup>	1.0739	0.0016 <sup>8</sup>	0.9734	1.0017	878.4	921.8	-43.4
0.08144	0.0065 <sup>8</sup>	1.1260	0.0047 <sup>3</sup>	0.9555	1.0049	828.7	891.0	-62.3
0.1324	0.0175 <sup>3</sup>	1.2114	0.0125 <sup>9</sup>	0.9279	1.0136	759.9	830.2	-70.3
0.1813	0.0328 <sup>7</sup>	1.2978	0.0236 <sup>0</sup>	0.9021	1.0262	703.2	755.9	-52.7
0.2253	0.0507 <sup>6</sup>	1.3801	0.0364 <sup>5</sup>	0.8791	1.0415	658.5	691.7	-33.2
0.2633	0.0693 <sup>3</sup>	1.4549	0.0497 <sup>8</sup>	0.8595	1.0579	624.6	648.2	-23.6
0.3095	0.0957 <sup>9</sup>	1.5514	0.0687 <sup>8</sup>	0.8359	1.0823	588.1	603.1	-15.0
0.3516	0.1236	1.6450	0.0887 <sup>4</sup>	0.8147	1.1089	559.0	567.5	- 8.5
0.3917	0.1534	1.7400	0.1101	0.7948	1.1385	534.8	538.7	- 3.9
*0.4371	0.1911	1.8555	0.1372	0.7725	1.1776	510.4	510.2	+ 0.2*
0.4764	0.2270	1.9633	0.1630	0.7534	1.2164	491.8	489.2	+ 2.6
0.5107	0.2608	2.0641	0.1873	0.7370	1.2541	476.9	474.0	+ 2.9
0.5426	0.2944	2.1643	0.2114	0.7220	1.2928	464.3	463.6	+ 0.7
0.5731	0.3284	2.2672	0.2358	0.7076	1.3332	452.8	453.3	- 0.5
*0.6148	0.3780	2.4203	0.2714	0.6884	1.3943	438.2	437.9	+ 0.3*
0.6510	0.4237	2.5670	0.3042	0.6719	1.4527	425.6	424.9	+ 0.7
0.6812	0.4640	2.7019	0.3332	0.6582	1.5062	415.1	413.0	+ 2.1
0.7173	0.5145	2.8808	0.3694	0.6421	1.5753	402.0	399.2	+ 2.8
0.7547	0.5696	3.0921	0.4090	0.6255	1.6539	387.2	381.4	+ 5.8
0.7687	0.5909	3.1796	0.4243	0.6195	1.6849	381.0	380.8	+ 0.2
0.8192	0.6711	3.5463	0.4819	0.5977	1.8063	355.7	355.2	+ 0.5
*0.8692	0.7555	4.0283	0.5425	0.5764	1.9412	321.8	322.6	- 0.8*
0.9006	0.8111	4.4369	0.5824	0.5633	2.0339	292.8	296.9	- 4.1
0.9344	0.8731	5.0557	0.6269	0.5494	2.1411	229.9	259.5	-29.6
0.9615	0.9245	5.8490	0.6638	0.5383	2.2332	198.2	221.7	-23.5

$$q_0 = \frac{2 \times 505,3}{0,546} = 1851 \text{ Gr. cal.},$$

PERSON found for the latent heat of solidification for tin

$$14,252 \times 118,5 = 1689 \text{ Gr. cal.}$$

The difference is so small, that we may assume also here that the *silver* is present as *atom* also in *tin*. This conclusion is the more justified as HEYCOCK and NEVILLE give for  $x$ : "somewhat smaller than 0,0385", from which follows that  $\theta$  will be somewhat greater and  $q_0$  somewhat smaller, so that  $q_0$  approaches still more to 1690.

I draw attention to the fact, that the good agreement of the value for *tin* found by PERSON justifies the conclusion that this value is really rather accurate, so that we must assume that the *mercury* (see my previous communication), solved in tin, is present in partially associated condition, the association amounting to about 1,5. It appeared namely that — when mercury did not occur in the solid phase, which consisted therefore exclusively of tin — the value of  $\theta$  was such, that it yielded  $q_0 = 2550$ . In order to make this value  $1\frac{1}{2}$  times smaller,  $\theta$  must be augmented, i. e.  $x$  must be diminished, and this can only be done by assuming association to the same amount.

V. Let us now return to the question of the *point of inflection* on the melting-point curve. From:

$$T = T_0 \frac{1 + \frac{ax^2}{(1+rx)^2}}{1 - \theta \log(1-x)}$$

follows

$$\frac{dT}{dx} = -\frac{T_0}{N^2} \frac{\theta}{1-x} \left( 1 + \frac{ax^2}{(1+rx)^2} \right) + \frac{T_0}{N} \cdot \frac{2ax}{(1+rx)^3},$$

therefore

$$\begin{aligned} \frac{d^2T}{dx^2} &= \frac{T_0}{N^2} \frac{\theta}{(1-x)^2} \left( \frac{2\theta}{N} - 1 \right) \left( 1 + \frac{ax^2}{(1+rx)^2} \right) - \\ &- 2 \frac{T_0}{N^2} \frac{\theta}{1-x} \frac{2ax}{(1+rx)^3} + \frac{T_0}{N} \frac{2a(1-2rx)}{(1+rx)^4}, \end{aligned}$$

or

$$\begin{aligned} \frac{d^2T}{dx^2} &= \frac{T_0}{N^2} \left[ \frac{\theta}{(1-x)^2} \left\{ \left( \frac{2\theta}{N} - 1 \right) \left( 1 + \frac{ax^2}{1+rx^2} \right) - \frac{4ax(1-x)}{(1+rx)^3} \right\} + \right. \\ &+ \left. \frac{2aN(1-2rx)}{(1+rx)^4} \right] \dots \dots \dots (3) \end{aligned}$$

If  $a=0$ , this equation may be written:



$$\frac{2}{-\log(1-x)} - 1 = 0, \quad \text{or} \quad -\log(1-x) = 2,$$

from which we find:  $x=0,865$ . If however  $a$  is not zero, then the equation  $-\log(1-x) = 2$  transforms the above equation into the following one:

$$\frac{1}{(1-x)^2} \left\{ -\frac{4ax(1-x)}{(1+rx)^3} \right\} + \frac{4a(1-2rx)}{(1+rx)^4} = 0,$$

or

$$1-2rx = \frac{x}{1-x} (1+rx),$$

which is only true, if

$$r = \frac{\frac{1}{x} - 2}{2-x} = \frac{1,156-2}{2-0,865} = -0,744.$$

We happened to find exactly  $r = -0,74$  for tin-mercury, so if  $\theta$  had been equal to  $\infty$  — the point of inflection would have been found at  $x=0,865$ .

Negative values of  $\theta$  (or  $q_0$ ) are required in order to find a point of inflection between that value of  $x$ , for which we find the point of inflection with  $\theta = \infty$ , and  $x=1$ . These negative values will occur very seldom, if at all. The principle result of the above investigation is therefore that the melting-point curve — the case of mixed crystals being excluded — will show a *point of inflection* if

$$\theta^2 - \frac{1}{2}\theta + a > 0,$$

or,  $\theta$  being equal to  $\frac{RT_0}{q_0}$  and  $a$  to  $\frac{\alpha_1}{q_0}$ , if

$$\frac{R^2T_0^2}{q_0} - \frac{1}{2}RT_0 + \alpha_1 > 0,$$

i. e. if

$$q_0 < \frac{2RT_0}{1 - \frac{2\alpha_1}{RT_0}}.$$

As  $R$ , expressed in Gr. Cal., amounts to 2, the condition may finally be written:

$$q_0 < \frac{4T_0}{1 - \frac{\alpha_1}{T_0}}, \quad \dots \dots \dots (5)$$

where  $q_0$  represents the latent heat (in Gr. Cal.) of the metal, which is deposited in solid condition,  $T_0$  the absolute melting temperature and  $\alpha_1 = \alpha q_0 = \frac{a_1 b_2^2 - 2a_{12} b_1 b_2 + a_2 b_1^2}{b_1^3}$ , also expressed in Gr. Cal.

As the quantity  $\frac{\alpha_1 v^2}{(1+rv)^2}$  represents in general the heat, which is given out pro molecule when an infinitely small quantity of the pure molten metal is mixed with the fluid metal mixture, the quantity  $\alpha_1 v^2$  will represent that same quantity of heat for  $v = 0$ .

We must here notice that the *accurate* values of  $\theta$  and  $q_0$  must be used, as well in equation (4) as in (5). So in the case of tin-mercury for instance  $\theta = 0,396$  is accurate only if the mercury is solved into the tin as atom. If this is not the case — and in the example mentioned we have every reason to suppose that the mercury is associated to an amount of 1,5 — then  $\theta$  must undergo a proportional *increase*.  $\theta$  was namely calculated from  $\theta = \frac{\angle T}{T_v}$ . If we apply the condition in the form (5), then we must substitute the *experimentally* determined value of the latent heat for  $q_0$ .

So in the case of tin-mercury  $\theta$  will not be equal to 0,4 but in reality to 0,6, and therefore  $\theta^2 - \frac{1}{2}\theta + a = 0,36 - 0,30 + 0,04 = 0,10$ , from which the existence of a point of inflection appears still clearer than in the supposition  $\theta = 0,4$ .

If we apply condition (5),  $\alpha_1$  being equal to  $0,0453 \times 1690 = 77$  Gr. Cal., we have certainly

$$1700 < \frac{4 \times 505}{1 - \frac{77}{505}}$$

If  $\alpha_1$  is *positive*, as is the general case, then the simple condition

$$\underline{q_0 < 4 T_0}$$

will include condition (5). This latter form therefore will provide us in nearly all cases with a reliable criterion whether or not a point of inflection occurs in the melting-point curve.

### Physiology. — “On the epithelium of the surface of the stomach.”

By Dr. M. C. DEKHCYZEN and Mr. P. VERMAAT. Veterinary surgeon. (Communicated by Prof. C. A. PEKELHARING).

We are accustomed to regard the stomach in the very first place as an organ for the *digestion* of food, for the preparation of the gastric juice. About its power of *resorption* its not so much is known. Glucose, peptones, strychnin, alcohol, dissolved in or diluted with water, are resorbed by the gastric mucous membrane. The rapidity of resorption is different in various kinds of animals. The structure of the cells which

line the mucous membrane seem to point to secretion of mucus more particularly than to resorption. The fact is that their peripheral portion readily undergoes a radical change, whereby it swells and is expelled as a lump of gastric mucus. Unless the utmost speed presides at the fixation of the gastric mucous membrane from any animal, the epithelium cells, which are still living but insufficiently fed, undergo intense changes when coming in contact with the by no means indifferent gastric juice. Until lately the epithelium cells of the stomach were thought by many to be open mucus cells, a kind of cylindrical goblet cells, because the above mentioned peripheral part, the so called "Lump of BIEDERMANN"<sup>1)</sup> had disappeared and only the cell-walls, which were more resistant, were left.

Improved means of fixation and chiefly also the fact that histologists have gradually been brought to see the necessity of a speedy fixation of perfectly fresh material, have been the cause that at least the open epithelium cell of the stomach has been acknowledged to be an artefact and it has been generally adopted that those cells are closed at their peripheral extremity by a smooth, convex boundary layer<sup>2)</sup>.

Starting from the supposition that microscopical investigation might bring to light something about the resorbing qualities, when the perfectly fresh gastric mucous membrane, is treated very rapidly with favorable means of fixation, a few young mammals and also older ones, which received milk along with their food, were killed by a single stroke on the head and the stomach was extracted without delay, turned inside out and immediately immersed into FLEMMING'S well-known mixture of  $\frac{3}{4}$  pCt. chromic acid, 5 pCt. acetic acid and  $\frac{2}{5}$  pCt. osmiumtetroxid. White rats and mice (full grown), a rabbit of 3, one of 15 days and one rabbit of 24 days nourished with milk, were taken for the experiments.

It now become evident that a comparatively small number of the epithelium-cells of the surface of the stomach contained *small drops of fat*: at least fine globules, which were colored black with  $\text{OsO}_4$  and agreed perfectly in size and appearance with those, which were visible in great numbers in the gastric contents, which had stuck to the mucous membrane in different places of the section. The surface of such gastric cells was not smooth either, but covered with a differentiation which resembled the striated border of the fatresorbing epithelium-cells of the intestine.

<sup>1)</sup> W. BIEDERMANN. Sitzungsberichte der Wiener Ak. d. d. Wiss. Mathem. naturw. Klasse. 71 Bd. S. 377. 1875.

<sup>2)</sup> K. W. ZIMMERMANN. Beiträge zur Kenntniss einiger Drüsen und Epithelien. Arch. f. mikrosk. Anatomic. Bd. 52. 1898. S. 552.

In the rabbit and the mouse small differentiations of the mucous membrane occur between the orifices of the pyloric glands as well as between those of the fundus glands, to which no better name could be given than that of *villi of the stomach*: slightly prominent, blunt elevations, rich in blood-capillaries and supported by a meshwork of connective adenoid tissue, but in which nothing of a central chyle-vessel, nor of smooth muscle-fibres could be detected. They were clothed with a single layer of cylindric epithelium, of which the cells, situated on or in the neighbourhood of the upper part of such a gastric villus carried outside of the above-mentioned boundary layer of the modern histologists, an *outer limb*, which seemed to consist of closely packed fibrils, probably cell-processes.

Each cell has its own apparatus; at the edges of the cells, where the "Schlussleisten" lie between the cells, the fibrils are wanting. Tangential sections of the upper part of those epithelium-cells of the stomach (sections of  $1\ \mu$  were studied) showed finely speckled pentagonal and hexagonal figures, separated by pretty wide furrows. They were stained violet with diluted RIBBERT'S phosphormolybdenous hematein.

The length of these bundles of cell-filaments is rather different in the various cells, but for one single cell pretty regular; they form externally gently convex lines; each cell is, as it were lined with a dome-shaped rather thick covering. There is not the least doubt that we have *not* to deal with adhesive gastric contents. These lie *on* these dome-shaped elevations and are separated from it by a small interstice, which was probably originally caused by shrinking during the process (alcohol, carbondisulphide, paraffine, etc.)

The different "outer limbs" of the cells may be grouped between two extremes: on the one side the extended cell-processes are seen to diverge more or less, best to be compared to a short brush with diverging hairs; on the other side we notice the pseudopodia drawn in, settled like stiff little hairs on the cell "membrane", and then such an outer limb resembles the well-known striated border of the resorbing epithelium-cells, or expressed in a more neutral expression: the surface-epithelium of the intestine.

These epithelium-cells of the stomach with outer limbs now show in the preparations a peculiarity at their base which has been noticed and photographed by CARLIER<sup>1)</sup>, but the reality of which has been doubted amongst others, by VON EBNER in KÖLLIKER'S

<sup>1)</sup> E. W. CARLIER. On intercellular bridges in columnar epithelium. La Cellule, XI. p. 263. 1896.

handbook<sup>1)</sup>. Tangential cuttings of  $1\ \mu$  of the basal extremities of the cells show us a picture, which agrees in high degree with the intracellular little bridges which may be seen to diverge in thin sections between the smooth muscle-cells (also in our preparations of the gastric wall). In other words the aspect reminds one of that of the rificells in the rete malpighii. If it be taken for granted that all this is preformed, then the opinion of CARLIER could be accepted that the epithelium-cells of the surface of the stomach are conic with their points turned towards the stroma of the cellular tissue, that they are mutually connected through fine cell-filaments, between which an extensive system of ducts to convey the juices might be supposed to be present "Saftkanälchen". On good grounds however histologists somewhat hesitate to accept the preformation of such structures. They *might* be post-mortal striking phenomena, or perhaps contractions during agony, or both.

However this may be, it is a fact that we have *not* observed them in the intestinal villi of the duodenum of the same animals; the epithelium-cells there were cylindrical, they firmly closed together at their basis and had a distinct low striated border. Never could these two kinds of cells: the resorbing epithelium-cells of the stomach and those of the duodenum be mistaken for one another; but they have some resemblance. The differentiations: the outer limbs and the striated border are probably nothing else but variations of one and the same cellorgan, which we meet with to a large extent in the intestine of invertebrate and vertebrate animals: a lining, which in the case of *Ascaris megalocephala*, shows the most striking resemblance to a ciliated lining, but in which we could *not* notice the *slightest* motion, though we worked under the most favorable circumstances and had quite fresh animals, which moved about intensely. Also in man ZIMMERMANN (l. c. fig. 37) has represented the striated border of the cells of the colon, which bore cellprocesses strikingly resembling cilia, but not considered by him as such either. We are of opinion that the intestinal cells and at least *some* cells of the surface of the stomach, possess the power to send out a great number of cell-filaments, which stand closely together when the striated border is contracted and when the cellfilaments have their minimumlength, but which can also be extended and are then enabled to diverge. The different heights of the striated border may also be seen in intestinal epithelium cells.

The outer limbs of the epithelium-cells of the stomach are evidently vulnerable differentiations. In some parts of our preparations

<sup>1)</sup> A. KÖLLIKER'S Handbuch der Gewebelehre des Menschen. 6e Aufl. III. 1. S. 155.

some of them have been converted into a homogenous hyaline mass, with distinct inward and outward boundary. Not that the external portions had become hyaline *bubbles*, their shape seemed little changed, but they were in a way "verquollen" as the German histologists say.

We must refrain from expressing an opinion whether these outer limbs are present in all epitheliuncells or not. It is quite possible that they are much more widely spread than we suspect and that they are frequently destroyed by imperfect fixation. Manipulating correctly and applying the same methods, we were not successful in obtaining a view of them on the surface of the stomach of a small suckling cat.

In studying the literature of the subject, we have found out that at the early date of 1856 a man of KÖLLIKER'S importance has seen globules of fat in the epitheliuncells of fresh gastric mucous membranes of young cats, dogs and mice. KÖLLIKER communicated on the 28<sup>th</sup> of June 1856 to the *Würzburger physikalisch-medicinische Gesellschaft* (VII p. 175) in a small paper entitled: "Einige Bemerkungen über die Resorption des Fettes im Darne, über das Vorkommen einer physiologischen Fettleber bei jungen Säugethieren und über die Function der Milz" that in his opinion he had seen globules of fat and also rather distinct indications of pores. With these pores he meant the openings in the "Porenmembran", the sieve-shaped, pierced, thickened wall of the cell, which we now call "striated border."

As far as we know no attention has been paid to this communication of KÖLLIKER'S, except by OGNEW (*Biologischer Centralblatt* XII, S. 689, 1892) who has also seen the structures of CARLIER. To our mind it is indisputable that the stomach can resorb fat from the food, although it be in small quantities and it is also probable that this excellent naturalist has been able to discern with simple means, what cannot, with the methods of the present time, be effected without difficulty: namely to point out the striated border-shaped outer limbs of the stomach cells.

**Physiology.** — "*On the liberation of trypsin from trypsin-zymogen.*"

By Dr. E. HEKMA. (Communicated by Prof H. J. HAMBURGER).

I. *On the influence of acids on the liberation of trypsin from trypsinogen.*

As is well-known, trypsin, the proteolytic digestive ferment of the pancreas, does not appear as such in this gland, but in the form of an inactive precedent stage, which HEIDENHAIN, to whom we owe this discovery<sup>1)</sup> has named "zymogen".

<sup>1)</sup> R. HEIDENHAIN, Beiträge zur Kenntniss des Pankreas, PFLÜGERS Archiv 1875, pag. 557.

As besides trypsin, other enzymes have come to our knowledge which are also secreted when in a preliminary stage, it is preferable, as is frequently done now, not to speak here of "zymogen", but of "trypsinogen" or "protrypsin".

From the very beginning the question arises whether the liberation of the ferment takes place in the gland or in the intestine. According to researches made by CAMUS and GLEY<sup>1)</sup> and DELEZENNE<sup>2)</sup>, the latter is usually the case; according to POPIELSKI<sup>3)</sup> always.

Then the second question arises: In what way does *the liberation in the intestine* take place?

Until a few years ago this liberating action was solely ascribed to the acid of the gastric juice.

Influenced by researches made in PAWLOW'S laboratory, attention has of late been drawn to the intestinal juice<sup>3)</sup>.

As there appeared to be two ways that might effect the liberation of trypsin, it was important to know, what relative value could be ascribed to each of them. I have therefore made the action of acids, amongst others also of hydrochloric acid, a subject of close investigation.

Tracing the communications in literature in respect to the influence of acids on the liberation of trypsin, one is always being directed to the publication of R. HEIDENHAIN, just mentioned. When we examine these writings we find that scarcely a page has been dedicated to this problem. Only the method, by means of which HEIDENHAIN has obtained the result, is shortly referred to, positive experiments are not described however. *He only mentions, that, when he had arrived at the end of his investigations; he found that glycerine-extracts from pancreassubstance operate much more effectively when the gland-substance is mixed with acetic acid, before glycerine is added; an observation which never failed in any of the cases when he applied this method.*

When a man like HEIDENHAIN publishes his observations, we have to take them into account, even although the experiments are not published along with them. In different text- and handbooks and monographs, we find related that acids possess the power to effect

<sup>1)</sup> CAMUS and GLEY; DELEZENNE. C. R. Soc. de Biol. LIV. (1902).

<sup>2)</sup> L. POPIELSKI, Ueber die Grundeigenschaften des Pankreassaftes. Centralbl. für Physiol. 9 Mai 1903.

<sup>3)</sup> N. P. SCHEPOWALNIKOW, Diss. Petersburg 1899; PAWLOW, Das Experiment. Wiesbaden 1900, p. 15; WALTHER, Archives Ital. de Biol. 1901.

H. J. HAMBURGER and E. HEKMA, "On intestinal juice of man." Report Royal Academy of Sciences 1902, p. 713.

the transformation of trypsinogen into trypsin, resp. of promoting it <sup>1)</sup>).

*I have been perfectly able to confirm HEIDENHAIN's investigations, but systematic researches have shown me, that they are only available for glycerine-extracts from the gland, but in no wise for watery extracts or for the pressed out juice of the pancreas.*

From the great number of experiments which I have made to this end, and which always led to the same results, I shall state here a single series.

First a repetition of HEIDENHAIN's experiment. The method which HEIDENHAIN indicates is as follows:

To every gram of pancreas substance, which has been cut into small pieces and subjected to pressure, is added 1 c.c. acetic acid of 1<sup>o</sup>/<sub>100</sub>. The mass is again rubbed for 10 minutes, and the thus obtained compound then mixed with 10 grams of glycerine. After 3 days this compound is filtered. I now composed a glycerine-extract according to this prescription and, along with this, other glycerine-extracts whereby instead of 1 cc. acetic acid of 1<sup>o</sup>/<sub>100</sub>, I took respectively 1 c.c. acetic acid of 2<sup>1</sup>/<sub>2</sub> <sup>o</sup>/<sub>100</sub>, 1 c.c. acetic acid of 0.5 <sup>o</sup>/<sub>100</sub> and 1 c.c. water.

The hereby obtained extracts I allowed to act on white of egg without water (Col. II) and also after addition of water (Column III) <sup>2)</sup>.

It is seen that where the glycerine-extracts of Col. I are brought to act on white of egg no digestion appears after 3 days (Col. II). This had to be expected. Even if trypsin had been set free, it could not have worked actively in the pure glycerine; for it is well-known that trypsin is not soluble in pure glycerine. Trypsin is liberated however when the glycerine-extracts are diluted with water (Col. III) and *more so* with those extracts which are composed with acetic acid (1, 2, 3) *than in those where ordinary water was used* (4). The acetic acid therefore furthers the liberation of the trypsin in glycerine-mixtures with water. A proportion between the concentration of the acetic acid and the extent of its operative power, does not exist however.

It could now be suggested that the trypsin from Col. III in Table I, which was at first inactive being in an indissoluble condition, now

<sup>1)</sup> I only mention here: HAMMARSTEN, Lehrbuch der physiol. Chemie, 1899. 4er Druck, pag. 295.

A. GAMGEE, (Deutsche Ausgabe von ASHER und BEYER), Die Physiol. Chemie der Verdauung, 1897, pag. 231.

C. OPPENHEIMER, Die Fermente und ihre Wirkungen, 1900, p. 74 and 116.

<sup>2)</sup> For the quantitative determination of the proteolytic digestion the method of MERT was followed. The experiments were only made with pig's pancreas. The temperature of the incubator varied from 37 to 39° C.

TABLE I.

I.	II.	III.
	Millimeters of white of egg consumed.	Millimeters of white of egg consumed after addition of 5 cc. water on 1 cc. extract, after the first 3 days.
	After 3 days.	After the following 3 days.
1). Pancreas substance 1 gram Acetic acid of 1 <sup>0</sup> / <sub>0</sub> 1 c.c. } 3cc. Glycerin 10 c.c.	0	4.50 + 4.70 } 4.70 + 4.80 } 18.70
2). Pancreas substance 1 gram Acetic acid of 2 <sup>1</sup> / <sub>2</sub> <sup>0</sup> / <sub>0</sub> 1 c.c. } 3cc. Glycerin 10 c.c.	0	4.40 + 4.60 } 4.70 + 4.60 } 18.30
3). Pancreas substance 1 gram Acetic acid of 0.5 <sup>0</sup> / <sub>0</sub> 1 c.c. } 3cc. Glycerin 10 c.c.	0	4.80 + 5 } 4.90 + 5 } 19.70
4). Pancreas substance 1 gram Water 1 c.c. } 3cc. Glycerin 10 c.c.	0	2.10 + 2.80 } 2.20 + 2.80 } 8.50

became active because of the addition of water. Table II shows however that in the original glycerin-extract, not diluted with water, *no* trypsin *whatever* was present.

In the experiments mentioned in Table II, a  $\text{Na}_2\text{CO}_3$  sol. of 1.2<sup>0</sup>/<sub>0</sub> has namely been added to the glycerin-extracts. If indeed trypsin had been set free, we might here have expected digestion of white of egg. The trypsin operates very effectively in presence of  $\text{Na}_2\text{CO}_3$  of 1.2<sup>0</sup>/<sub>0</sub>, whereas the latter entirely prevents the transformation of trypsinogen into trypsin; a fact, already proved by HEIDENHAIN and which I have taken advantage of in all my experiments to prove, whether in certain cases I had to deal with material containing trypsin or trypsinogen.

From these figures we notice that 1 cc. acetic acid in concentrations of resp. 1, 2<sup>1</sup>/<sub>2</sub> and 0.5<sup>0</sup>/<sub>0</sub> has not the power, just like 1 cc. water, to liberate trypsin from 1 gram of pancreas substance in the

TABLE II.

		Millimeters of white of egg consumed.	
		After 3days	After 6days
1). Pancreas substance	4 gram	0	0
Acetic acid of 4 $\frac{0}{10}$	1 cc. } 3 cc. + 12 cc. Na <sub>2</sub> CO <sub>3</sub> opl. v. 4.2 $\frac{0}{10}$		
Glycerin	40 cc. }		
2). Pancreas substance	4 gram	0	0
Acetic acid of 2 $\frac{1}{2}$ $\frac{0}{10}$	1 cc. } 3 cc. + 12 cc. Na <sub>2</sub> CO <sub>3</sub> opl. v. 4.2 $\frac{0}{10}$		
Glycerin	40 cc. }		
3). Pancreas substance	4 gram	0	0
Acetic acid of 0.5 $\frac{0}{10}$	1 cc. } 3 cc. + 12 cc. Na <sub>2</sub> CO <sub>3</sub> opl. v. 4.2 $\frac{0}{10}$		
Glycerin	40 cc. }		
4). Pancreas substance	4 gram	0	0
Water	1 cc. } 3 cc. + 12 cc. Na <sub>2</sub> CO <sub>3</sub> opl. v. 4.2 $\frac{0}{10}$		
Glycerin	40 cc. }		

time (mentioned by HEIDENHAIN), during which these liquids had come into contact with the pancreas substance, before glycerin was added<sup>1)</sup> It is however possible, as has been proved from Table I, to liberate trypsin *from the glycerin-extracts* by means of water, after having been brought into contact with it for a lengthened period and this process is aided by acetic acid being present. But the action of acetic acid is only of indirect nature, *it only seems to neutralize in some degree the unfavourable action which glycerin exerts on the liberation of trypsin.*

Then I thought, if this be the case, the favorable action of the acetic acid must fail to be effective in watery extracts and pressed out juice of the pancreas. This proved to be true, as table III and IV will show.

<sup>1)</sup> It should be observed that 1 cc. acetic acid, resp. water and 1 gram pancreas substance only give the relative proportions. In reality 5 cc. liquid on 5 grams pancreas substance was always taken and of course 50 cc. glycerin.

TABLE III.

Fresh Panc. juice. Two drops.		Directly	After 48 hours.		After 40 hours.	
		Reaction litmus- paper.	Reaction litmus- paper.	Millimeters of white of egg consumed.	Reaction litmus- paper	Millimeters of white of egg consumed.
1	fresh P. juice + 5 cc. acetic acid 2 1/2 %	acid	acid	0	acid	0
2	» + 5 cc. » 1 %	»	»	0	»	0
3	» + 5 cc. » 0.5 %	»	»	0	»	0
4	» + 5 cc. » 0.1 %	»	»	0	»	0
5	» + 5 cc. » 0.05 %	»	»	0	weak ac.	$\frac{1.10+1.10}{1.10+1.20}$ 4.40
6	» + 5 cc. water	neutral	neutral	0	weak alk.	$\frac{1.40+1.30}{1.20+1.30}$ 5.20
7	» + 5 cc. Na <sub>2</sub> CO <sub>3</sub> sol. 0.1 %	alkaline	alkaline	0	alkaline	$\frac{1.20+1.10}{1.20+1.10}$ 4.60
8	» + 5 cc. » 0.5 %	»	»	0	»	$\frac{0.10+0.10}{0+0}$ 0.20
9	» + 5 cc. » 1 %	»	»	0	»	0
10	» + 5 cc. » 1.5 %	»	»	0	»	0
11	» + 5 cc. » 2 %	»	»	0	»	0
12	» + 5 cc. » 3 %	»	»	0	»	0
13	» + 5 cc. Extract from the intestinal mucosa <sup>1)</sup>	neutral	weak alk.	$\frac{1.90+1.80}{1.81+1.80}$ 7.30	weak alk.	$\frac{4+4.10}{4+4}$ 16.10

Table III shows us, that when a few drops of fresh, pressed out pancreas juice, which according to fig. 9, 10, 11 and 12 contained no trypsin, are mixed with acetic acid of 2 1/2, 1, 0.5 and 0.1 %, there is no digestion of white of egg. But when the acetic acid is used more diluted, viz. 0.05, then after a long time, formation of trypsin takes place, but not to a greater extent than when water is taken instead of acetic acid.

It could now be supposed that the trypsin would, under the influence of the acetic acid be liberated, but could not operate actively in the present acid reaction. Table IV shows that this is partly the case. For when an old pancreas is taken, in which according to 9,

<sup>1)</sup> Extract from the intestinal mucosa may be used for the liberation of trypsin instead of the natural intestinal juice. In a following communication we expect to treat this subject more fully.

TABLE IV.

Juice of a pancreas which has been exposed for 24 hours to room-temperature. Two drops.			Directly.	After 18 hours.		After 40 hours.	
			Reaction litmus-paper.	Reaction litmus-paper.	Millimeters of white of egg consumed.	Reaction litmus-paper.	Millimeters of white of egg consumed.
1	old P juice	+ 5 cc. acetic acid 2 1/2 %	acid	acid	0	acid	0
2	"	+ 5 cc. " 1 %	"	"	0	"	0
3	"	+ 5 cc. " 0.5 %	"	"	0	"	0
4	"	+ 5 cc. " 0.1 %	"	"	1.30+1.30 1.40+1.40 } 5.40	"	3+3 3+3 } 12
5	"	+ 5 cc. " 0.05 %	"	"	1.70+1.70 1.70+1.70 } 6.80	weak ac.	3.40+3.30 3.30+3.20 } 13.20
6	"	+ water	neutral	weak alk.	2+2.10 2+1.80 } 7.90	weak alk.	3.70+3.70 3.80+3.80 } 15
7	"	+ 5 cc. Na <sub>2</sub> CO <sub>3</sub> sol. 0.1 %	alkaline	alkaline	1.50+1.60 1.50+1.60 } 6.20	alkaline	3.20+3.40 2.90+2.90 } 12.10
8	"	+ 5 cc. " 0.5 %	"	"	1.50+1.50 1.40+1.50 } 5.90	"	2.9+2.80 2.80+2.70 } 11.20
9	"	+ 5 cc. " 1 %	"	"	1.20+1.30 1.30+1.30 } 5.10	"	2.60+2.70 2.60+2.70 } 10.60
10	"	+ 5 cc. " 1.5 %	"	"	1.20+1.30 1.30+1.30 } 5.10	"	2.40+2.40 2.50+2.60 } 9.90
11	"	+ 5 cc. " 2 %	"	"	0.90+0.9 ) 1+1 ) 3.80	"	1.90+2 ) 1.80+1.70 } 7.40
12	"	+ 5 cc. " 3 %	"	"	0.50+0.50 ) 0.50+0.50 ) 2	"	1+1.20 ) 1.10+1.20 } 4.50
13	"	+ 5 cc. Extract from the intestinal mucosa	neutral	weak alk.	2.40+2.60 2.60+2.50 } 10.10	weak alk.	4.40+4.30 4.20+4.20 } 17.10

10, 11 and 12 free trypsin is found and according to Table III, acetic acid has been added of 2 1/2, 1 and 0.5 %, there is no action whatever. The acid in these concentrations prevents the trypsin from acting. When however acetic acid of 0.1 % is used, then the action of the trypsin is not neutralized as is shown in Table 4, fig. 4. Therefore in fig. 4, Table III, *the liberation of trypsin must have been prevented by acetic acid of 0.1 %.*

Moreover Table III teaches us that in no single case digestion of white of egg was obtained with fresh pancreasjuice after 18 hours, except in fig. 13.

Hereby is clearly shown that water and acetic acid of 0.05 % are

far behind intestinal mucosa, resp. intestinal juice, with regard to their influence of liberating trypsin from trypsinogen.

Equal results as with acetic acid were obtained with *hydrochloric acid*, *lactic acid* and *butyric acid*. For hydrochloric acid this may appear from the following summary.

TABLE V.

Fresh pancreasjuice, two drops.	Millimeters of white of egg consumed.		Digest. of white egg after once more $2 \times 24$ hours in 6 and 7.
	After 17 hours.	After 41 hours.	
1) pancreasjuice + 3 cc. water	0	$\begin{matrix} 1.80+1.70 \\ 1.70+1.90 \end{matrix} \left. \vphantom{\begin{matrix} 1.80+1.70 \\ 1.70+1.90 \end{matrix}} \right\} 7.10$	
2) » + 3 cc. $\text{Na}_2\text{CO}_3$ opl. 1 %.	0	0	
3) » + 3 cc. extr. from the intestinal mucosa.	$\begin{matrix} 1.60+1.50 \\ 1.50+1.50 \end{matrix} \left. \vphantom{\begin{matrix} 1.60+1.50 \\ 1.50+1.50 \end{matrix}} \right\} 6.10$	$\begin{matrix} 4+4.20 \\ 4+4.10 \end{matrix} \left. \vphantom{\begin{matrix} 4+4.20 \\ 4+4.10 \end{matrix}} \right\} 16.30$	
4) » + 3 cc. $\text{HCl}$ 0.02 $\frac{1}{2}$ %.	0	$\begin{matrix} 1.70+1.80 \\ 1.70+1.70 \end{matrix} \left. \vphantom{\begin{matrix} 1.70+1.80 \\ 1.70+1.70 \end{matrix}} \right\} 6.90$	
5) » + 3 cc. $\text{HCl}$ 0.05 %.	0	$\begin{matrix} 1.70+1.60 \\ 1.60+1.60 \end{matrix} \left. \vphantom{\begin{matrix} 1.70+1.60 \\ 1.60+1.60 \end{matrix}} \right\} 6.50$	
6) » + 3 cc. $\text{HCl}$ 0.1 %.	0	0	0
7) » + 3 cc. $\text{HCl}$ 0.5 %.	0	0	0

These figures show that hydrochloric acid in extremely weak concentrations (0.02 $\frac{1}{2}$  and 0.05 %) does not hinder the trypsin from being set free. The effect is not favourable however. Somewhat stronger concentrations of hydrochloric acid (0.1 %, 0.5 %) prevent the liberation of trypsin entirely. That no trypsin has been set free in 6 and 7, the action of which may have been prevented by the hydrochloric acid, has been proved from the fact that no digestion of white of egg had occurred, even after  $2 \times 24$  hours, when after 41 hours a solution of  $\text{Na}_2\text{CO}_3$  had been added to the liquids named in 6 and 7, until the proportion of  $\text{Na}_2\text{CO}_3$  amounted to circa 1 %.

From these researches we may with certainty draw the following conclusions.

- 1) HEIDENHAIN'S opinion, which has been current since 1875 and

widely accepted, as if acids could have the power of liberating trypsin from trypsinogen is not correct; on the contrary, they prevent this liberation.

2) That HEIDENHAIN came to this conclusion must be ascribed to the accidental occurrence, that instead of using the pressed out juice or watery extracts of the pancreas, he had taken glycerin-extracts from the gland. The favorable action caused by the presence of acetic acid in his experiments and which I have been able to confirm, is to be ascribed to the fact that acetic acid decreases the injurious action of the glycerin on the liberation.

3) As it has now been proved that the gastric juice does in no wise further the liberation of trypsin, but rather opposes it, we may therefore draw the conclusion, *that in this process of liberation all the work falls to the intestinal juice; a fact still increasing in importance where the investigations of POPIELSKI have proved, that no free trypsin whatever appears in the pancreassecreta, but that it is only there in the shape of trypsinogen.*

Having arrived at the end of my communication, I beg Prof. HAMBURGER to accept my warm thanks for the opportunity afforded to me to make these researches and also for the useful hints kindly given to me.

*Physiological laboratory of the State University at Groningen. May 1903.*

**Physics.** — *“Some remarks on the reversibility of molecular motions.”*

By Dr. A. PANNEKOEK. (Communicated by Prof. H. A. LORENTZ).

1. The following considerations deal chiefly with the question whether a mechanical explanation of nature is possible. Mechanics treat the motion of discrete particles or of continuous masses; now the question may be raised, whether all natural phenomena can be explained by means of such a motion. In other words, it is the question, whether or no we know particular properties of these phenomena, which exclude the possibility of a mechanical explanation of general application. A particular property which seems to do so, is the irreversibility of the natural phenomena, the change in a definite direction. When investigating whether this is really the case, we need only consider the simplest form in which the irreversibility of natural phenomena occurs: the second law of the mechanical theory of heat.

POINCARÉ says about this in his "Thermodynamique", that it entirely excludes the possibility of a mechanical explanation of the universe.

The motions of which mechanics treat, are all reversible: there occur only forces which depend on place, so relations between the 0<sup>th</sup> and the 2<sup>nd</sup> derivative according to time: if the sign of  $t$  is reversed, these equations retain their validity. It is true that in mechanics also cases are treated in which the first derivative according to  $t$  occurs in the equations (friction): we are, however, justified in calling these cases not purely mechanic, because in them heat is produced, so that in a complete explanation we must introduce considerations (thermodynamic ones), which we are just trying to solve in purely mechanic ones. It is therefore desirable to call only those cases *purely* mechanic which are *reversible*; these only are conservative. In the above-mentioned not purely mechanic cases there is dissipation of energy, so that, the law for the conservation of energy being a general law of nature, a mechanical description of them is not complete. The kinetic theory of gases shows us that this description only mentions the visible motions in the system, but not the molecular motion, which is required to make the description complete. The word mechanic, occurring in the question raised in the beginning must therefore be interpreted in such a way that we consider only cases of conservative systems as purely mechanic.

The question whether the irreversibility of the natural phenomena *decisively excludes* a mechanical explanation, must be answered in the negative, when we succeed in giving a mechanical description of one typical and simple irreversible process, or in other words, if we can point out in a certain case that a process consisting of purely mechanic, so reversible motions, is irreversible. We must then at the same time get an insight into the question, how it is in general possible, that a process in its general character can be so different from that of the partial processes of which it consists.

2. BOLTZMANN has shown that we meet with such a case, though an abstract one, when we have a perfect gas, consisting of perfectly elastic spheres, between which no other forces act than those eventuating in collisions between two particles. He proved that the function  $H = \int f \log f d\omega$ , in which  $f d\omega$  is the number of the molecules whose points of velocity lie in the volume element  $d\omega$  of the velocity diagram<sup>1)</sup>, can only be made smaller, never greater by the collisions.

1) The "velocity diagram" is obtained by representing the velocity of every molecule by a vector drawn from a fixed point. This vector ends in the "point of velocity" of this molecule.

As this function taken with the reversed sign, expresses at the same time the logarithm of the "probability" of a certain distribution of the velocities, BOLTZMANN expresses his result also under the following form: the effect of the collisions is that a gas always gets from a more improbable to a more probable condition.

Here we have therefore a process, consisting of purely mechanic partial processes, which shows change in one direction only. That however BOLTZMANN's considerations have not yet led to a perfectly satisfactory insight, and that this contrast is felt as a contradiction, is proved by the objections and doubts, which have been adduced against these considerations without refuting them. Let us assume a fictitious system in which at the moment  $t_0$  all the places are the same, but all the velocities exactly the opposite of those of the real system. The two systems can represent a gas in exactly the same way, there being no possibility of seeing which is the real and which the fictitious one. Yet the fictitious one will successively pass through all the conditions through which the natural one has passed before the time  $t_0$ , in reverse order; all the collisions take place in opposite direction, and the system gets from a "more probable" to a "more improbable" condition.

BOLTZMANN denies that this involves a contradiction, for the fictitious system is "*moleculär-geordnet*". That this remark does not solve the difficulty (BRILLOUIN, among others, expressed doubts as to this in a note in the French translation of BOLTZMANN's *Vorlesungen*) must be ascribed to the fact, that the ideas "ordered" and "unordered" for molecular motions are difficult to define sharply. Sometimes ordered is interpreted as if it meant that in the fictitious system to every molecule its future course is accurately prescribed. This however is not satisfactory. If we know at the moment  $t_0$  the places and velocities of the natural system, we are enabled to determine beforehand, so to prescribe, the future course for the natural and for the fictitious system and for both in exactly the same way.

The fact that the motions in the fictitious system are ordered can be better pointed out by means of the following consideration. If we take two groups of molecules with the points of velocity  $P_1$  and  $P_1'$ , which come into collision, then after the collision the points of velocity  $Q_1$  and  $Q_1'$ ,  $R_1$  and  $R_1'$  etc., will all lie on a sphere of which the line  $P_1P_1'$  is a diameter. The places of  $Q, R, \dots$  on the sphere depend on the direction of the planes of collision  $A, B, \dots$ ; to every plane of collision belongs a definite place of the points of velocity and the latter are scattered all over the sphere, because the former have all kinds of directions. If we now take the reversed,

fictitious system, all these points of velocity come back in  $P_1P_1'$ , because *definite* planes of collision  $A, \dots$  belong to every pair of points of velocity  $Q_1Q_1' \dots$ . The fictitious system, therefore, is subjected to the *condition*, that molecules with definite points of velocity do not collide according to arbitrarily chosen planes or to planes whose direction is determined by chance, but according to planes which are entirely *determined* by the position of these points of velocity. This condition may be called an ordering of the motions.

We must, however, add another remark. In the natural system we had not only points of velocity in  $P_1P_1'$ , but also at the ends of the other diameters of the sphere  $P_2P_2', P_3P_3' \dots$  etc. and these too can reach the same points  $Q_1Q_1'$  as  $P_1P_1'$ , if only the planes of collision have every time the required direction different from  $A$ . Of all the points of velocity and planes of collision we have just now chosen and considered separately all those which in the natural system lie before, in the fictitious system after the collisions in  $P_1P_1'$ . We might, however, just as well have chosen and considered separately those which in the natural system lie after, in the fictitious system before the collision in  $Q_1Q_1'$ ; in this case we might have been inclined, to call the fictitious system unordered, and the natural system ordered. The difference between the two would of course become clear, when we paid attention to the *number* of collisions which cause the points of velocity to pass from  $P_1P_1'$  to  $Q_1Q_1', R_1R_1'$  etc. or vice versa. In reality the collisions in the natural system have a scattering effect, through which the distribution of the points of velocity over the sphere is more regular and arbitrary after impact than before. In this respect there is a real difference between the natural and the fictitious system, that in the former the distribution before the collision is more irregular, less accidental. The difference between being ordered and unordered in the molecular motions in the two systems appears here as a difference in the degree of the ordering.

It seems to me that though we cannot bring forward conclusive objections against the denomination used by BOLTZMANN, yet further considerations which throw some light on these phenomena, might be of some value.

3. The ordering of the motions, in which the difference between the natural and the fictitious system consists, can only be clear, when, as in the kinetic theory of gases, we examine larger masses and mean values, in which the coordinates and velocities are considered as fluently varying quantities. When we take the particles separately, in which the coordinates and velocities are perfectly defined, the

difference between a natural and a fictitious system does not appear, and the process can only be taken as perfectly reversible.

The result of each of the steps of which the whole process is built up (free path + collision), is determined 1<sup>st</sup> by the coordinates and velocities, 2<sup>nd</sup> by the direction of the normal to the collision plane. In the statistical method of treatment of the kinetic theory of gases the latter is considered as an independent datum, which therefore is thought to be defined by chance; we may then give it different values, which are distributed according to chance, i. e. regularly, and in this way the scattering, regulating effect of the collisions appears, which is the cause of the irreversibility of the process. In the purely mechanic conception, in which we must take the condition of every separate particle as rigorously defined, the direction of the normal is no independent datum; in reality this direction is accurately defined by the coordinates and the velocities of the colliding particles. Here the result is therefore determined by the coordinates and the velocities only and according to this way of considering the question, the process must be considered to be reversible.

The question how it is possible that a process may be considered in two ways, so totally different comes therefore to the same as the question, how quantities which in reality are rigorously determined by other quantities, may yet be considered to be independent and determined by chance.

We shall find the answer to this question in the fact, that very small variations in the coordinates and velocities bring about considerable variations in the direction of the normal. If we determine the directions by means of the points in which they cut a spherical surface described with a radius equal to the mean free path, the velocities being measured by the path covered in the mean time interval between two collisions, and if we call the ratio between the radius of a molecule and the mean free path a small quantity of the first order, then we may formulate this proposition more precisely as follows: variations of a given order of smallness in the coordinates and the velocities bring about variations in the direction of the normal which are of one order lower; variations in the direction of the normal give rise to variations of the same order in the coordinates and the velocities after impact.

If we ascribe to the coordinates and the velocities of two colliding molecules values  $x_1 y_1 z_1 x_2 y_2 z_2 u_1 v_1 w_1 u_2 v_2 w_2$  which are rigorously determined, then the direction of the normal  $\lambda \mu \nu$  is also rigorously determined. If however we mean by these 12 data that these quantities

lie between  $x_1$  and  $x_1 + dx_1$  etc. . . .  $w_2$  and  $w_2 + dw_2$ , i. e. that the condition is included in a twelve-dimensional volume element of the first order, then  $\lambda$ ,  $\mu$  and  $\nu$  are left undefined. This way of proceeding is that of the kinetic theory of gases in which we are therefore justified in considering the normal to the tangent plane of two colliding molecules to be determined by chance.

If we wish to know this direction accurate to the first order, then the 12 coordinates and velocities must be known to the second order. If within this volume element we determine the place by means of new coordinates  $x_1' y_1' z_1' \dots v_2' w_2'$ , (we might call them coordinates of the 2<sup>nd</sup> class) which vary within that element over a finite region, e. g. from 0 to 1, then the direction  $\lambda \mu \nu$  is a function of these coordinates of the second class, and they determine the 12 coordinates and velocities after impact also to the first order.

Every collision brings about a lowering of the order of determination of the coordinates and the velocities; every collision causes a scattering by which the condition of the system becomes one order less determined. In order to know the condition (the coordinates and the velocities) after  $n$  collisions (at least accurate to quantities of the first order) we must know the initial values of the coordinates and the velocities accurate to the  $(n + 1)$ <sup>th</sup> order. The longer the period is for which we want to predict the motion, the higher is the order which is required for our knowledge at this instant. The limit is here the pure mechanic conception, according to which the state is determined for ever, because the data are determined with absolute accuracy.

BOLTZMANN'S observation, that a system, whose motion is reversed really proceeds from a more probable condition to a less probable one, namely to that from which the natural system started, and that afterwards conditions are reached, which show again an increasing probability, includes the assumption, that in the initial state the coordinates and the velocities were determined to the  $(2n + 1)$ <sup>th</sup> order, so that the reverse motion brings the system after  $n$  collisions back to the initial volume element of the first order; afterwards the direction of the normal is no longer determined, and the further process must be investigated according to the rules of the calculus of probabilities. The condition whose validity is required for the proof of the  $H$ -theorem, is not satisfied during the whole backward course of the process; it is here therefore impossible to decide anything as to the decrease or increase of  $H$ . As soon as the initial state is again reached the direction of the normal ceases to be determined, and the required condition is satisfied. From the further course we may therefore predict with certainty, that  $H$  must decrease.

The observation may here be inserted, that we speak of chance in nature, when small variations in the initial data occasion considerable variations in the final elements, because we cannot observe those small variations. Cyclic motions for instance will also always give rise to such cases.

For the special case considered here the result we have found may be formulated as follows: when in a purely mechanic, reversible process which occurs a great many times in the same way, events occur in which small variations in the initial data occasion considerable variations in the final state, then the total process gets the properties of an irreversible process.

**Botany.** — “*On a Sclerotinia hitherto unknown and injurious to the cultivation of tobacco.*” (*Sclerotinia Nicotianae* OUD. et KONING).  
(By Prof. C. A. J. A. OUDEMANS and Mr. C. J. KONING).

The following communication contains five paragraphs.

*Par. I* gives an account of a visit to the tobaccofields in the Veluwe and Betuwe, in the autumn of 1902, about the time that the tobaccoleaves begin to be gathered.

*Par. II* contains an investigation of the disease which had attacked the plants, evidently a fungus, which had long been known as “Rot”, but the nature of which had not yet been cleared up.

*Par. III* gives a summary of the experiments made with the Sclerotia of the fungus.

*Par. IV* deals with the anatomy of the Sclerotia and the *Sclerotinia* produced from them.

*Par. V* contains the result of some biochemical investigations.

*Par. VI* gives a few hints, the application of which may prevent or reduce the damage caused by *Sclerotinia Nicotianae*.

#### I. A VISIT TO THE TOBACCOFIELDS.

In order to study more closely the origin of the well-known patches and specks on dried tobaccoleaves, one of us repeatedly visited the tobaccofields in the Veluwe and Betuwe in September 1902. These visits repaid the trouble very well indeed, as they gave an opportunity of becoming acquainted with an evil which caused much damage, had not yet been clearly defined and so deserved a closer study.

In these visits one was first of all struck by the fact that the very extensive fields under cultivation were divided into smaller square

plots by beanhedges and that these hedges consisted partly of scarlet-runners (*Phaseolus coccineus* = *Ph. multiflorus*) and partly of "curved-beak" (a variety of French beans *Phaseolus vulgaris* SAVI<sup>1)</sup>).

On account of their height these plants were considered effective as windscreens. Tobacco leaves namely, by their large surface as well as by their tender structure, cannot very well stand air-currents, which is proved by the fact that the scouring or rubbing of two leaves against each other by the wind, may cause discoloured spots, bruising of the tissues and even loss of substance.

Though the method of protecting the tobaccoplant against wind had evidently been well chosen, yet the growers themselves had noticed that it was wrong to use two different kinds of *Phaseolus*, because diseased tobaccoplants are much more frequent within hedges of scarlet-runners than of French beans. Experts are certainly right in their opinion that the reason of this is that scarlet-runners retain their leaves much longer than French beans. The latter begin to lose their leaves already in September and October, when the season can already be rather damp, whereas the scarlet-runners show no sign of it yet then. Hence the soaked soil as well as the damp plants can much better be dried by the wind within the hedges of French beans than of scarlet-runners. Accordingly the "rot" is in damp years always much stronger inside the leafed than inside the leafless hedges.

Another drawback of scarlet-runners is that their flower-clusters have not yet fallen off in September and October, so that, after having died, they not unfrequently drop down on the tobaccoplants and soaked through, remain hanging in the axils and in other places, where like wet sponges they foster the germination of conidia or spores.

In a visit to the tabaccofields of Mr. N. VAN OS at Amerongen on Sept. 27, 1902, many plants were found suffering from "rot". As such the growers considered specimens with limp, slippery leaves and with stems having discoloured stains. This was supported by the experience that such leaves and stems possess very infectious properties and that a single diseased leaf, carried to the drying-shed under a big heap on a wheelbarrow, can in one night easily infect some fifty others. Any precise idea of the agent here at work, was not found however among the experts, so that the only means of

<sup>1)</sup> The tobacco-growers themselves informed us that hedges of beans, especially of scarlet-runners and "curved-beaks" as windscreens, have been in use on tobacco fields as far back as can be remembered. In accordance with this they are mentioned by the late Prof. VAN HALL on page 60 and 61 of his "Landhuis-houdkundige Flora" dating from 1855.

arriving at a scientific result was to take parts of sick plants to the laboratory and to study them there.

Meanwhile a continued walk through the tobaccofields had revealed that this was a case not of a bacterial disease as had originally been supposed but of a sclerotial disease, since in various places in a greater or less degree spots were found on leaves and stems consisting of a white down and besides greater or smaller black grains, embedded in or lying on that down, so that on account of other observations made elsewhere, it seemed probable that these black organisms under favourable conditions might produce an ascigerous generation, from the morphological properties of which the place of the fungus in the system and its identity or difference with other known species might be inferred.

The richest crop of material for experiments was gathered in the dampest places, i. e. in the corners of hedges of scarlet-runners, while on the other hand in the vicinity of French beans often not a single grain was to be found. Where flowers or flower-clusters of scarlet-runners were held fast in the axils of tobaccoleaves, sclerotia were rarely sought in vain. It can be understood that the uninitiated — growers and working-men — imagined that the source of the evil had entirely to be sought in the blossoms of the scarlet-runners.

## II. INVESTIGATION OF THE DISEASE WHICH HAD ATTACKED THE PLANTS.

On various days of September 1902 sick parts of stems and leaves were taken home from the tobaccofields as well as from the drying sheds. In doing so each leaf and each stem were separately put into a sterilised tube and in the laboratory placed into a sterilised glass-box over wet filtering paper.

At a temperature of 22° C. a distinct change could already be observed in all the objects after 24 hours. They had developed a flimsy, transparent, much-branched mycelium. At a lower temperature the same phenomenon had occurred though less vigorously.

After 3 × 24 hours small bits of the obtained net of threads were with the necessary precautions placed on malt-gelatine and kept at 22°. Already after 24 hours these bits had grown much and it was possible after another 24 hours to take away new bits from the margin of the circular cultures which had now grown to a diameter of 3,5 centimeters and to inoculate them on freshly prepared malt-gelatine. In this way a sufficient quantity of pure cultures were obtained in a relatively short time.

As healthy tobacco-plants were largely at our disposal, it was

possible to carry the downy substance on them and to place the infected parts of leaves and stems in damp glass-boxes at 22° C. Again a beginning growth was noticeable after 24 hours.

The pure cultures on the malt-gelatine plates became more and more extensive, forming circles which after three days had diameters of 8, after four days of 13 centimeters.

By and by the malt-gelatine was peptonised and in a smaller or greater number of places, near the margin more than in the middle of the circles, small, white, glossy points arose, which secreted drops of a colourless, quite clear liquid, but which required no more than 12 hours to turn into black dots. These also continued the process of drop-formation for some time, when after some further increase in size they changed into shorter or longer, round or angular little bodies, which clearly belonged to the class of sclerotia. Having grown more and more independent of the hyphae which at first occluded them, these black bodies could now be removed without damaging them and they appeared to have reached a maximum length of 10 millimeters and a thickness of 5–6 millimeters.

The experiments on infection with parts of living tobaccoplants were all successful on condition that the place of inoculation was kept very wet, e.g. by wrapping it up in very wet cottonwool or some woodshavings steeped in water. The attacked tissues became discoloured also here.

From what precedes we may infer that the fungus cultivated on malt-gelatine does not differ from that of the tobaccofields, which was irrefutably proved later when from the sclerotia of both the same *Sclerotinia* was obtained.

It is worth mentioning that the myceliumcultures on the malt-gelatine which had produced the sclerotium, had besides given rise in several places to dull white, granulated spots, which microscopical examination revealed to consist of 1<sup>st</sup>. clusters of flask- or cone-shaped conidiophores, borne by erect or ascending hyphae and 2<sup>nd</sup>. a number of curious crystals pressed against the thread-shaped cells, partly loosely spread, partly assembled in clusters.

The colourless conidiophores were high 12–16  $\mu$  and broad 4–5  $\mu$  and consisted of a cylindrical body tapering a little towards the lower end, a thinner short neck and a spherical head, which latter just slightly exceeded the neck in breadth and produced spherical colourless conidia of 2.5  $\mu$  diameter, which were at first connected to short chains, but soon broke up and commenced an individual existence.

The crystals and other bodies, often striated, not occluded in cells,

of varying shape and size, soluble in diluted hydrochloric acid in which they left a structureless residue, soon appeared to belong to the class of "calcospherites": organic compounds of calcium treated by the late Professor P. HARTING in 1872 in a quarto Treatise of the Royal Academy of Sciences, entitled: "Morphologie Synthétique sur la production artificielle de quelques formations calcaires organiques".

There could be no doubt that these calcospherites stood in no relation to the fungus, but had been produced by the gelatine, while on the other hand, the presence of conidia proved that the new *Sclerotinia*, like other species of the same genus, could multiply by conidia as well as by ascospores.

On the maltgelatine-plates which had been exposed to the air of the tobaccofields and in the drying-sheds, the same mouldy spots developed under the most favourable conditions of the laboratory, which had drawn our attention on the stems and leaves in the fields, and which had afterwards been artificially multiplied. More important still is that somewhat later the same sort of *Sclerotia* developed, the germination and further development of which gave origin to the formation of apothecia.

There cannot be the least doubt that the conidia floating in the air, by settling on the gelatine-plates, had produced the infection and the ensuing phenomena, so that these last experiments throw a clear light on the possibility of extensive tobaccofields being ruined in a very short time, as soon as by a prevailing uncommonly damp condition of the atmosphere a small patch of mould has anywhere found occasion to develop threads. At the same time they show that the opinion of VON TAVEL (Vergl. Morph. der Pilze, 1892, p. 105): "Es (die Arten von *Sclerotinia*) sind parasitische Pilze, deren Sclerotien im Innern der Pflanzentheile sich bilden ganz nach Art einer *Claviceps*" cannot be admitted for *Sclerotinia Nicotianae*, and that here an ectogenous formation of the *Sclerotium* has been substituted for an endogenous one.

### III. CULTIVATION-EXPERIMENTS APPLIED TO *SCLEROTIUM NICOTIANAE*.

The sclerotia whose development it was desired to study were buried in sand, garden-soil, forest-soil and leaf-earth respectively, placed in suitable dishes partly in daylight, partly in dark, and after having been properly watered exposed to various temperatures among which that of 22° C. Not earlier than 6 weeks later the first sign of new life was observed in the shape of numerous black-brown

little hills with a lighter-coloured top. The earliest appearance was in the dishes filled with forest-soil and placed in daylight at 15° C., whereas a temperature of 22° C. seemed to have hindered development. The culture in sand always remained backward. The hills gradually assumed the shape of little rods, but took 3—4 months to reach the appearance of thin little stems or threads, bent down over the surface. These latter moved in the direction of light.

The number of threads varied widely for the different grains (Fig. 2 and 5), but did not exceed 20. The progress of the growth was at first very small indeed (2 millimeters in 40 days) and was even insignificant between Nov. 1902 and Febr. 1903. But then the threads rapidly grew in length and in March measured as much as 6 centimeters.

After the thickness of the sprouts had very long remained unchanged, at last (in March) a distinct swelling appeared at their top, which at first club-shaped rounded and closed, soon divided into a somewhat inflated neck (apophysis) and a broader disc-shaped terminal piece, which latter could easily be recognised as an open shallow apothecium with the edge slightly bent inward (Fig. 8). The correctness of this view appeared when the microscopical examination had revealed the presence of spore-bearing asci and paraphyses in the disc (Fig. 9).

A single sclerotium appeared to be able to bear some six well-developed apothecia and besides some dwarfish rods.

Unburied Sclerotia do not develop, although they remain resting on the bed of mycelium-threads which produced them. Cultures in Petri-dishes were mostly spoiled by bacteria.

Bits of a fruit-stem, grown from a Sclerotium buried in humus, when placed on malt-gelatine gave origin to the development of white pads, which in their turn sometimes produced new Sclerotia in a week's time. Bits of white Sclerotial flesh behaved similarly.

The fungus-generation grows very rapidly on malt-gelatine as well as on bits of tobaccoplants at 22° C., though its temperature optimum is at about 24° C. At 37° C. the growth is arrested. Between 15° and 20° C. the development is still satisfactory.

#### IV. ANATOMICAL INVESTIGATION.

The mouldy threads which in the field develop on the surface of green parts of plants and which afterwards produce the Sclerotia, grow equally in all directions and so gradually form white discs, of increasing diameter, finally reaching an average breadth of 2 centimeters. These threads are colourless, 2  $\mu$  thick, much ramified, repea-

iedly septate, filled with a finely granulated protoplasm and occasionally accompanied by threads five times thicker, the significance of which could not be discovered.

From the thinner, creeping fibres others rise up on which either singly or in small clusters, flask- or cone-shaped organs develop, whose function is to split off conidia and which hence deserve the name of conidiophores. They are on an average  $15 \mu$  high and  $3.5 \mu$  broad and consist of a thick body, tapering a little at the bottom, a short, thick neck and a spherical head, only slightly thicker than the neck. From the spherical or knob-shaped head colourless, spherical conidia of  $2.5 \mu$  diameter come forth, which are very soon detached from each other, but the multiplication of which goes on for a very long time, as may be inferred from their extremely large number.

The Sclerotia, externally black, internally white, diverge little from the common type as far as their structure is concerned. They consist of a pseudoparenchym the cells of which are somewhat bigger in the middle of the grains, somewhat smaller near the surface, show various, mostly distorted shapes (fig. 7), have very thick walls and are not separated by intercellular spaces. The walls of the more superficial cells are black, of the more central ones colourless. If a sclerotium rests with part of its surface against the glass of a tube or box, the black colour does not develop there.

The spore-bearing generation (fig. 8) which under favourable conditions comes forth from not too old Sclerotia and consists of a long, thread-shaped stem and a miniature apothecium, shows, in the first-mentioned part short, cylindrical or column-shaped, closely packed cells, which at the surface bend dorsally, but in doing so assume the shape of clubs or retorts and turn their broadest part outside. They have a light-brown shade and impart to the stems and cups a peculiar appearance as if they were covered with downy scales.

The hymenium consists of asci and numerous loosely packed paraphyses, of which some protrude a little above the others (Fig. 10). The asci are tubular, with rounded tips, insensible to iodine,  $160-180 \times 6-7 \mu$  and contain in their  $\frac{2}{3}$  upper parts 8 inclined, colourless, oval spores in a single row. The paraphyses are only slightly swollen at the top and almost colourless. Germinating spores were not seen.

#### V. BIOCHEMICAL INVESTIGATION.

In order to study the conditions of life of *Sclerotinia Nicotianae*,

the fungus was cultivated on and in different nutritive materials of known composition.

It appeared in the first place that the presence of free oxygen is absolutely necessary for its growth; with anaerobic methods of cultivation according to BUCHNER and LABORUS no trace of development took place. It is not improbable that this is the reason why the mycelium only grows extremely slowly in nutrient liquids, where the quantity of oxygen below the surface is necessarily small.

On the other hand the fungus appeared to grow very rapidly when inoculated on malt-gelatine, malt-agar and also on parts of leaves and stems of the tobaccoplant, sterilised at a high temperature. Then a woolly mycelium developed, in some places rising above the surface. Below the surface of liquids or filtrates, obtained from parts of stems or leaves, after inoculation with the fungus, only a meagre cloudy mycelium appeared. As soon however as part of this had reached the surface of the liquid, its growth became much more vigorous. In some cases a floating sclerotium was even produced.

Next the influence of the reaction of the nutrient liquid was studied. In a solution of 0.1% of potassium nitrate, 0.5% glucose, 0.050% magnesiumsulphate and 0.050% potassiummonophosphate, containing carbon and nitrogen assimilable by the fungus, *Sclerotinia Nicotianae* does not easily support free acid or alkali. The acid limit lies with this solution at about 1 cubic centimetre of  $\frac{1}{10}$  normal sulphuric acid to 100 cubic centimetres of liquid, and the alkaline limit at 0.5 cM<sup>3</sup> of  $\frac{1}{10}$  normal potassiumhydrate. Neither limit can be sharply drawn as the fungus only slowly produces acid in the solution mentioned. With 1.5 cM<sup>3</sup>. of  $\frac{1}{10}$  normal sulphuric acid no growth whatever takes place any longer; with the alkaline solution the limit could not be sharply defined.

Moreover an elaborate investigation was made as to which compounds were profitable to the fungus as carbonaceous and which as nitrogenous foods. As a carbonaceous food glycese, as a nitrogenous one saltpetre in the above-mentioned concentration, proved most satisfactory. Ammonium nitrate, a very good nitrogenous food, was not available of course in the presence of alkalis.

In the further experiments the saltpetre was replaced by a similar quantity (0.1 %) of the nitrogen compound to be studied or the glycese by the carbon compound to be studied in the same concentration.

#### a. *Nitrogenous food.*

Nitrogen was offered to the fungus in the form of potassium

nitrate, potassium nitrite, chloride, nitrate, phosphate, sulphate, carbonate of ammonia and ammonia. Ammonium nitrate gave the best results. The other compounds showed little difference. Of ammonia which was added in very small quantities, hardly anything was assimilated.

Of amido compounds, which are generally known as good sources of nitrogen for fungi, glycocoll, asparagine, aspartic acid, alanine, tyrosine and leucine gave good results in the present case also. The nitrogen of urea, creatine, parabanic acid and uric acid has little nutritive value. From the last mentioned substance also carbon can be assimilated.

Among aromatic compounds, only the nitrogen of ammoniumsalts has any nutritive value; among the derivatives of pyridine only the nitrogen of the residue, not the carbon. To develop the fungus glucose has consequently to be added to the nutritive material. Nicotine, being a free alcaloid can serve as a source neither of nitrogen nor of carbon.

If assimilable carbon is present, the nitrogen is used from the ammoniumsalts of oxalic, tartaric, citric and benzoic acids, least from ammonium succinate.

#### b. *Carbonaceous food.*

Of fatty acids only very dilute acetic acid (0.050 %) has a nutritive value for carbon.

The polyacid alcohols are bad sources of carbon, as was shown by an investigation with glycerine, erythrite, mannite, sorbite, adonite and dulcitol. Least satisfactory was sorbite and also glycerine, a good carbon-food for many fungi, gave bad results here. Lactic acid in very small quantities, was available as a carbon-food.

Very differently behaved the sugars. As was already mentioned, glucose comes first in nutritive value. Besides were studied: arabinose, xylose, saccharose, fructose, maltose, lactose, raffinose and melibiose. Of all these only xylose and arabinose had any value as sources of carbon. In all other solutions only a trace of growth was observed. Though not without difficulty the fungus was able to derive carbon from cellulose. On filtering paper wetted with the above-mentioned nutrient solution, but without glucose, a snowwhite, woolly mycelium developed. Also from inuline carbon may be obtained.

#### c. *Nitrogenous and carbonaceous food.*

As mixed sources of carbon and nitrogen we must mention asparagine, aspartic acid and alanine. The addition of potassium nitrate

improved the growth more with aspartic acid than with asparagine, which must probably be ascribed to the two carboxylgroups, active as sources of carbon.

Finally it must be mentioned that also peptone can furnish carbon as well as nitrogen, but that the nutritive value for nitrogen is increased here by adding glycose.

In accordance with the results of KLEBS, it was found that a high nutritive value of the liquid had influence on the formation of Sclerotia with alanine, leucine, aspartic acid and glycose. These bodies appeared under the mentioned favourable conditions at the surface of the liquid in about three weeks' time.

#### VI. HINTS ABOUT THE PREVENTION OF THE SCLEROTINIA-DISEASE ("ROT") IN TOBACCOFIELDS.

As a damp soil and a damp atmosphere are both absolutely necessary for the development of the "rot" or *Sclerotinia*-disease and as this disease in wet years appears about the time when the tobacco-leaves begin to be gathered, it is absolutely necessary, for the reasons given above, to stop the cultivation of scarlet-runners (*Phaseolus coccineus*, also named *Phas. multiflorus*) on the tobaccofields and only to admit and to continue the cultivation of French beans (*Phaseolus vulgaris* SAVI).

Besides limp leaves or stems or such as are covered with the least quantity of a white down must immediately be removed and burned.

The leaves that have been carried into the drying-sheds must at once be laid asunder and hung up to be dried. Suspected leaves must be sorted out and destroyed.

#### DIAGNOSIS LATINA.

*Sclerotinia Nicotianae* Oul. et Koning. — *Sclerotii*s ad superficiem caulium et foliorum primo in compagine densissimo filorum mycelii niveorum absconditis, celeriter mole argentibus, mox itaque expositis, tandemque a substratu decidentibus, extus nigris, intus albis, nunc subglobosis, tunc iterum oblongis, 10 maxime mill. longis, 5—6 mill. maxime crassis, teretibus vel subangulosis. — *Ascomatibus* plurimis (usque ad 20) ab uno eodumque sclerotio protrusis, longe stipitatis, tenerrimis; stipite filiformi, tereti, flexuoso, 4—6 centim. longo, 1/2 mill. crasso, deorsum scabro, sursum laevi, summo obesiore, sic ut ascoma satis longe apophysatum videatur, una cum ascomate

pallide fuscescente, floccoso-squamuloso. *Ascomata* proprio minimo, primo coniformi, clauso; dein p. m. expansō, perforato; tandem patelliformi, late aperto, 0.8 mill. in diam., 0.2 mill. alto, margine incurvato. — *Ascis* cylindricis, apice rotundatis, iodo haud caerulescentibus, deorsum breve stipitatis,  $160-180 \times 6-7 \mu$ , paraphysibus obvallatis, octosporis. — *Sporidiis* ellipticis,  $5-7 \times 3-4 \mu$ , in partibus ascorum  $\frac{2}{3}$ , superioribus oblique monostichis, levibus, hyalinis.

*Paraphysibus* filiformibus, summo subelavatis, numerosissimis, dense congestis, ascos paullo superantibus,  $2\frac{1}{3} \mu$  crassis, protoplasmate dilute-fuscescente faretis.

Ex mycelii hyphis repentibus hyalinis, septatis, ramosis, numerosimae assurgunt hyphae basidiiferae; basidiis sive conidiophoris lageniformibus ut plurimum conglobatis, summo conidia sphaerica, hyalina, diam.  $2.5 \mu$ , in catenas breves coadunata procreantibus.

Conidia ex aëre in patellam gelatina praeparata repletam delapsa, mox germinare incipiunt, myceliumque proferunt, cujus hyphae, quum plurimis locis arctius inter se coalescant, sclerotiorum novorum exordia edunt.

#### EXPLANATION OF THE PLATES.

- Fig. 1. Four mature sclerotia ( $4-8 \times 3-4$  mill.), magnified.
- Fig. 2. Two Sclerotia with a certain number of sprouts (juvenile ascomata) magnified.
- Fig. 3. Microscopical representation of erect branches of the mycelium, against the top of which free calcospherites (from the gelatine) and also clusters of them have fastened.
- Fig. 4. Microscopical representation of lying and ascending mycelium-threads, with the conidiophores produced by them and the apical conidia and chains of conidia originated therefrom.
- Fig. 5. A Sclerotium with partly immature, partly full-grown long-stemmed Sclerotia, magnified.
- Fig. 6. Section of a Sclerotium, magnified.
- Fig. 7. Microscopical picture of part of a section of a Sclerotium.
- Fig. 8. Nearly full-grown and full-grown ascomata, of which one cut longitudinally, magnified.
- Fig. 9. Microscopical representation of part of a longitudinal section of a mature ascoma, with spore-bearing asci and paraphyses.
- Fig. 10. Part of Fig. 9. enlarged.
- Fig. 11. Top of an ascus and a couple of spores, still more enlarged.

**Physics.** — Dr. J. E. VERSCHAFFELT: "*Contributions to the knowledge of VAN DER WAALS'  $\psi$ -surface VII. The equations of state and the  $\psi$ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components.*" (part 3)<sup>1)</sup>. (Supplement N<sup>o</sup>. 6 to the Communication from the Physical Laboratory at Leiden by Prof. KAMERLINGH ONNES).

(Communicated in the meeting of Febr. 28, 1903.)

15. *The  $\psi$ -surface in the immediate neighbourhood of the plaitpoint.*

By the application, after KEESOM<sup>2)</sup>, of KORTEWEG's projective transformation<sup>3)</sup> to the equations of the  $\psi$ -surface, I have expressed the coefficients of my equation (20) in terms of those used by KORTEWEG to study the plait in the paper mentioned.

The following new coordinates must be introduced

$$\begin{aligned}\psi'' &= (\psi - \psi_{T_{pl}}) - (v - v_{T_{pl}}) \left( \frac{\partial \psi}{\partial v} \right)_{T_{pl}} - (x - x_{T_{pl}}) \left( \frac{\partial \psi}{\partial x} \right)_{T_{pl}}; \\ x'' &= (x - x_{T_{pl}}) - m (v - v_{T_{pl}}), \\ v' &= v - v_{T_{pl}}.\end{aligned}$$

where  $m$  is determined by the equation

$$m \left( \frac{\partial^2 \psi}{\partial v^2} \right)_{T_{pl}} + \left( \frac{\partial^2 \psi}{\partial x \partial v} \right)_{T_{pl}} = 0;$$

to the first approximation and by the use of equation (20) this reduces to

$$m = \frac{m_{v1}}{RT_k} x_{T_{pl}} \text{ } ^4).$$

Since the equation of the  $\psi$ -surface contains a term with  $\log x$ .

1) Proc. Amsterdam. 28 June and 27 Sept. 1902.

2) Proc. Amsterdam. 27 Sept. 1902, p. 341.

3) Wien. Ber., 98, 1159, 1889.

4) In agreement with KEESOM's expression (i.e. p. 342). The value of  $m$  must also fulfil the two other equations:

$$m \left( \frac{\partial^2 \psi}{\partial x \partial v} \right)_{T_{pl}} + \left( \frac{\partial^2 \psi}{\partial v^2} \right)_{T_{pl}} = 0$$

and

$$m^2 \left( \frac{\partial^2 \psi}{\partial v^3} \right)_{T_{pl}} + 3 m^2 \left( \frac{\partial^2 \psi}{\partial v^2 \partial c} \right)_{T_{pl}} + 3 m \left( \frac{\partial^2 \psi}{\partial v \partial v^2} \right)_{T_{pl}} + \left( \frac{\partial^2 \psi}{\partial v^3} \right)_{T_{pl}} = 0;$$

this is really the case when the above values of  $x_{T_{pl}}$  and  $v_{T_{pl}}$  are substituted. Conversely we can use these equations to determine  $x_{T_{pl}}$  and  $v_{T_{pl}}$ , as KORTEWEG has done. (Proc. Amsterdam. 31 Jan. 1903, p. 526).

it can only be identified with KORTEWEG's equation (2), when  $\log x$  can be expanded in a series. This can only happen when the difference between  $x$  and  $x_{T_{pl}}$  is so small that  $x - x_{T_{pl}}$  is vanishingly small with regard to  $x_{T_{pl}}$ . We remain thus in the immediate neighbourhood of the plaitpoint<sup>1)</sup>. In this case we find that the equation of the  $\psi$ -surface can be brought into the form

$$\psi'' = c_1 x''^2 + d_1 x''^3 + d_2 x''^2 v'' + d_3 x' v''^2 + e_1 x'^4 + \dots$$

where, to the first approximation

$$c_1 = \frac{1}{2} \frac{RT_k}{x_{T_{pl}}}, \quad d_1 = -\frac{1}{6} \frac{RT_k}{x^2_{T_{pl}}}, \quad d_2 = -\frac{1}{2} \frac{m_{01}}{x_{T_{pl}}},$$

$$d_3 = -\frac{1}{2RT_k} (m^2_{01} + RT_k m_{11}), \quad e_1 = \frac{1}{12} \frac{RT_k}{x^3_{T_{pl}}}, \quad e_2 = \frac{1}{3} \frac{m_{01}}{x^2_{T_{pl}}},$$

$$e_3 = \frac{1}{2} \frac{m^2_{01}}{RT_k x_{T_{pl}}}, \quad e_4 = \frac{1}{3R^2 T^2_k} (m^3_{01} - R^2 T^2_k m_{21}), \quad e_5 = -\frac{1}{4} m_{30}, \dots$$

$$f_4 = -\frac{1}{5} m_{40} \text{ etc. } ^2).$$

The expression  $4e_1 e_3 - d_3^2 = -\frac{1}{2} \frac{RT_k m_{30}}{x_{T_{pl}}}$  is always positive hence  $m_{30}$  is always negative; it follows that the plaitpoint on the  $\psi$ -surface is always of the first kind<sup>3)</sup>.

Since  $d_3 = 0$  when  $m^2_{01} + RT_k m_{11} = 0$ , the second special case of border curve and connodal line treated by me<sup>4)</sup> agrees with the

<sup>1)</sup> The following expansion can thus be used to determine the coordinates of the critical point of contact, (cf. KEESOM l.c. p. 342).

<sup>2)</sup> The expressions for  $d_3$  and  $e_5$  agree with those found by KEESOM (l. c. p. 341).

<sup>3)</sup> See KORTEWEG, Wien. Ber., p. 1158.

<sup>4)</sup> Proc. Amsterdam 27 Sept. 1902 p. 329. The reference to this special case allows me to correct some mistakes in the formulae which are connected with this and the preceding special cases. In Proc. of 28 June 1902 p. 267 line 2, read:

$$p_1 - pTk = \left( m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} \frac{m^2_{11} m_{40}}{m^2_{30}} \right) \Xi^2,$$

and in Proc. 27 Sept. p. 328, line 12:

$$p - pTk = \frac{m^2_{30}}{m^2_{11}} \left( m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} \frac{m^2_{11} m_{40}}{m^2_{30}} \right) (v - vTk)^4.$$

Further in the last Proceeding p. 329 line 9 for the coefficient of  $\frac{m_{01} m_{02}}{RT_k}$

read 4 instead of  $\frac{5}{2}$

first double-plaitpoint case of KORTEWEG<sup>1)</sup>. The second case for a double-plaitpoint, i. e.  $4c_1e_5 - d_3^2 = 0$ , does not occur on the  $\psi$ -surface.

### 16. Application to a particular equation.

In a communication published in the Proceedings of the Academy for 31 Jan. 1903, KORTEWEG has determined the plaitpoint and critical point of contact for mixtures with a small proportion of one component, but on the assumption that these mixtures satisfy VAN DER WAALS' equation of state

$$p = \frac{RT}{v-b_x} - \frac{a_x}{v^2},$$

where

$$a_x = a_1(1-x)^2 + 2a_{12}x(1-x) + a_2x^2$$

and

$$b_x = b_1(1-x)^2 + 2b_{12}x(1-x) + b_2x^2.$$

The formulae found by KORTEWEG can be immediately deduced from my formulae, when we introduce the special forms which my coefficients will then assume.

First we may note that, in this case, the critical constants for the homogeneous mixture are

$$T_{xk} = \frac{8}{27} \frac{a_x}{b_x R}, \quad p_{xk} = \frac{1}{27} \frac{a_x}{b_x^2} \quad \text{and} \quad v_{xk} = 3b_x,$$

<sup>1)</sup> l. c. p. 1166. In using the same method with KORTEWEG's equation (2), as I have used to determine the critical constants, I have found the following expression:

$$y_2 + y_1 = \frac{4c_1e_4e_5 + d_3^2e_4 - 4d_2d_3e_5 - 4c_1d_3f_6}{4e_5(d_3^2 - 4c_1e_5)} (x_2 + x_1),$$

$$(y_2 - y_1)^2 = -\frac{d_3}{e_5} (x_2 + x_1),$$

and

$$x_2 - x_1 = \frac{4d_2e_5^2 - 2d_3e_4e_5 + d_3^2f_6}{2e_5(d_3^2 - 4c_1e_5)} (x_2 + x_1) (y_2 - y_1).$$

where  $x_1, x_2, y_1$  and  $y_2$  are the coordinates of the ends of the tangent-chord.

In the special case when  $d_3 = 0$  we get

$$y_2 + y_1 = -\frac{1}{4} \frac{e_4}{e_5} (x_2 + x_1), \quad x_2 - x_1 = -\frac{1}{2} \frac{d_2}{c_1} (x_2 + x_1) (y_2 - y_1)$$

and

$$(y_2 - y_1)^2 = \frac{1}{2e_5} \left( \frac{d_2^2}{c_1} - e_3 + \frac{3}{8} \frac{e_4^2}{e_5} \right) (x_2 + x_1)^2.$$

By the introduction of the above values for the coefficients, my expressions for  $\Phi, \varphi$  and  $\xi$  are again found. The *first* approximation for  $d_2, c_1$  and  $e_3$  will then be certainly *insufficient* in the last expression.

so that KAMERLINGH ONNES' coefficients  $\alpha$ ,  $\beta$  and  $\gamma$  become

$$\alpha = 2 \left( \frac{a_{12}}{a_1} - \frac{b_{12}}{b_1} \right) , \quad \beta = 2 \left( 1 + \frac{a_{12}}{a_1} - 2 \frac{b_{12}}{b_1} \right) , \quad \gamma = 2 \left( \frac{b_{12}}{b_1} - 1 \right).$$

Further we find, by comparing my equation (18) with the above equation of state:

$$\begin{aligned} m_{01} &= \left( \frac{\partial p}{\partial v} \right)_{Tk} = \frac{2 a_1}{27 b_1^2} \left( 1 - 3 \frac{a_{12}}{a_1} + 2 \frac{b_{12}}{b_1} \right) \\ m_{11} &= \left( \frac{\partial^2 p}{\partial v \partial v} \right)_{Tk} = \frac{4 a_1}{27 b_1^3} \left( \frac{a_{12}}{a_1} - \frac{b_{12}}{b_1} \right) \\ m_{21} &= \frac{1}{2} \left( \frac{\partial^3 p}{\partial v^2 \partial v} \right)_{Tk} = - \frac{1}{27 b_1^4} \left( 1 + 2 \frac{a_{12}}{a_1} - 3 \frac{b_{12}}{b_1} \right) \\ m_{30} &= \frac{1}{6} \left( \frac{\partial^3 p}{\partial v^3} \right)_{Tk} = - \frac{1}{486} \frac{a_1}{b_1^5}. \end{aligned}$$

If these special values are substituted in my general formulae, KORTEWEG's special formulae are obtained, and in addition some which he has not given. These are not given here as they are not sufficiently simple and they can also be easily reproduced.

KORTEWEG has already given the results obtained from these formulae. I will here only remark that the special cases 1, 2, 3 and 4 of KORTEWEG's fig. 1 agree with my fig. 15 and the cases 5, 6, 7 and 8 with 14. As fig. 15 is obtained for the case that  $m_{01}^2 + RT_k m_{11} > 0$  and fig. 14 when  $m_{01}^2 + RT_k m_{11} < 0$ , the boundary between the two cases is determined by  $m_{01}^2 + RT_k m_{11} = 0$ , which in connection with the special equation of state can be written

$$\left( 1 - \frac{3 a_{12}}{a_1} + 2 \frac{b_{12}}{b_1} \right)^2 + 8 \left( \frac{a_{12}}{a_1} - \frac{b_{12}}{b_1} \right) = 0.$$

This is the equation of the parabolic border curve given by KORTEWEG.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday June 27, 1903.

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CONTENTS.

- H. W. BAKHUIS ROOZEBOOM: "The boiling-point curves of the system sulphur and chlorine", p. 63.
- A. SMITS and L. K. WOLFF: "The velocity of transformation of carbon monoxide" (II). (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 66.
- J. K. A. WERTHEIM SALOMONSON: "A new law concerning the relation between stimulus and effect." (Communicated by Prof. C. WINKLER), p. 73. (With one plate).
- Extract from the Report made by the Committee of advice for the awarding of the *Bruys Ballot*-Medal, p. 78.
- C. A. J. A. OUDEMANS and C. J. KONING: "On a Sclerotinia hitherto unknown and injurious to the cultivation of Tobacco (*Sclerotinia Nicotianae* OUD. et KONING). Postscript. p. 85. (With one plate).
- A. GORTER: "The cause of sleep." (Communicated by Prof. C. WINKLER), p. 86.
- C. A. LOBRY DE BRUYN and C. L. JUNGUS: "The condition of hydrates of nickelsulphate in methylalcoholic solution", p. 91.
- C. A. LOBRY DE BRUYN and C. L. JUNGUS: "The conductive power of hydrates of nickel-sulphate dissolved in methylalcohol", p. 94.
- C. A. LOBRY DE BRUYN: "Do the Ions carry the solvent with them in electrolysis", p. 97.
- C. L. JUNGUS: "The mutual transformation of the two stereo-isomeric methyl-*d*-glucosides." (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 99.
- S. TYMSTRA BZN.: "The electrolytic conductivity of solutions of sodium in mixtures of ethyl- or methylalcohol and water". (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 104. (With one plate).
- W. EINTHOVEN: "The string galvanometer and the human electrocardiogram", p. 107. (With two plates).
- J. E. VERSCHAFFELT: "Contributions to the knowledge of VAN DER WAALS'  $\psi$ -surface. VII. (part 4). The equation of state and the  $\psi$ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components". (Communicated by Prof. H. KAMERLINGH ONNES), p. 115. (With one plate).
- J. D. VAN DER WAALS: "The liquid state and the equation of condition", p. 123.
- J. J. VAN LAAR: "On the possible forms of the melting point-curve for binary mixtures of isomorphous substances." (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 151. (With one plate).

The following papers were read:

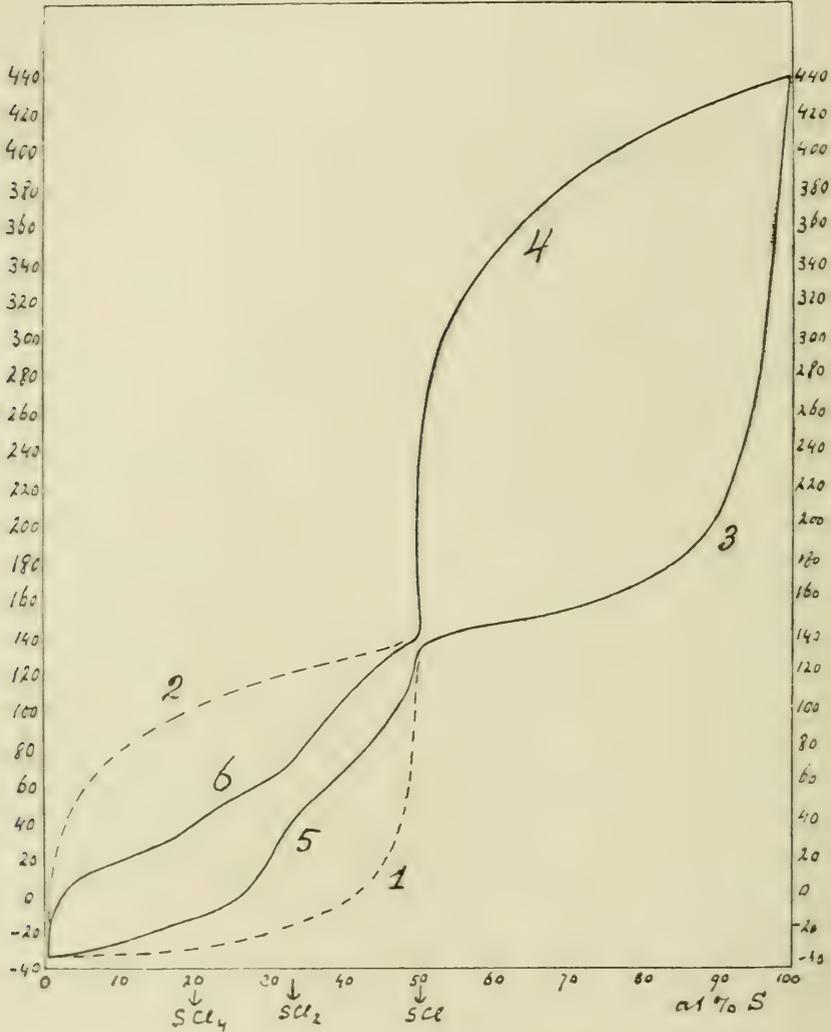
**Chemistry.** — "*The boiling-point curves of the system sulphur and chlorine.*" By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of May 30, 1903).

Binary systems in which the formation of complex molecules may be assumed to take place in a greater or smaller degree have been frequently investigated as regards the equilibria between a liquid

phase and solid phases, but hardly ever with regard to the equilibria between liquid and vapour.

I, therefore, proposed to further investigate this relation in the case of vapour pressure- and boiling-point curves on a series of



examples in which the nature and the degree of the complex molecules varied, in order to obtain a more definite idea of the changes which these curves undergo as compared with the simple case in which the binary system consists only of two kinds of molecules.

Such an example is furnished by the system sulphur-chlorine, the boiling-point curves of which are given in the accompanying figure, which is constructed from determinations made by Mr. ATEN.

Liquid sulphur and liquid chlorine are miscible in all proportions. If in these mixtures no compound molecules were formed, two regular boiling-point curves might be expected which would diverge very much in the centre because the boiling points of the two components lie far apart.

In these mixtures, however, a fairly stable compound  $S_2Cl_2$  is formed. If this compound were absolutely stable, that is if a liquid and a vapour of the composition  $S_2Cl_2$  consisted of nothing but molecules of this formula, then the liquid and vapour would at this point, have exactly the same composition. The system  $S+Cl$  would then in reality be compounded of the two systems  $S+S_2Cl_2$  and  $S_2Cl_2+Cl_2$  which could no doubt be represented in one figure, but then the liquid- and the vapour-pressure curves would not pass continuously into each other at the composition  $S_2Cl_2$ .

As it is known that the dissociation of the vapour of  $S_2Cl_2$  is small it may be anticipated that, in the system  $S+Cl$ , the connection at the composition  $S Cl$  might become continuous, but in such a way that the vapour and liquid curves nearly coincide at this point.

This state of affairs was now confirmed and is indicated in the figure by the liquid curve 1,3 and by the vapour curve 2,4. It will be seen that the curves 1 and 2 and 3 and 4 nearly meet in a point situated near the composition  $S Cl$ , but in reality we have here continuity, from which it appears that  $S_2Cl_2$  is not absolutely stable either in the form of liquid or vapour. The difference however, is so small that this type really exhibits one of the smallest forms of deviation.

In the case of binary mixtures where the compound formed is more strongly dissociated the divergence of the two curves at the point representing the compound will be much greater. The liquid curve and the vapour curve of the entire system will then more and more assume the form which in the figure belongs to both halves.

The investigation however, showed a further peculiarity in the lower half. The boiling-point curves 1 and 2 for the mixtures whose composition lies between  $Cl$  and  $S Cl$  only relate to mixtures which are freshly prepared from liquid  $S_2Cl_2$  and liquid chlorine.

These mixtures at temperatures below  $0^\circ$  retain for a very long time their yellow colour and then exhibit the boiling point lines indicated at 1 and 2. At higher temperatures, and very quickly above  $30^\circ$ , the colour becomes darker and finally blood red, chiefly in the case of mixtures approaching the composition  $S Cl_4$ .

The boiling points then rise, sometimes very considerably, to a maximum amount of about  $70^\circ$  so that the line 5 is found for the

definite boiling points of liquids which have reached their final equilibrium, which occurs after some hours at the ordinary temperature.

At the same time we get, in place of the vapour curve 2, the new vapour curve 6. As the velocity of reaction above  $40^\circ$  becomes very great, the lines 1 and 2 cannot be accurately determined above this temperature. For 1 this causes no inconvenience as its further course must be almost vertical, but the upper part of 2 becomes rather uncertain.

The final boiling-point curves 5 and 6 are situated much closer together than the first named one and have moreover an exceedingly irregular shape. It cannot as yet be decided whether this is solely attributable to the formation of  $\text{SCl}_4$  molecules in the mixtures, or whether other compound molecules are formed.

The formation of compound molecules may be noticed not only from the change of colour, but also from a diminution of the volume and will if possible, be studied quantitatively.

The important question in what manner the melting-point curve of solid  $\text{SCl}_4$  is modified by the presence of more or less compound molecules in the liquid phase is still the subject of investigation.

**Chemistry:** — *“The velocity of transformation of carbon monoxide IP”.*

By Dr. A. SMITS and L. K. WOLFF. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Communicated in the meeting of May 30, 1903).

In our previous paper on the above subject<sup>1)</sup> we communicated results obtained at the temperatures  $256^\circ$ ,  $310^\circ$  and  $340^\circ$ , from which we concluded that at these temperatures the transformation of CO into  $\text{CO}_2$  and C is unimolecular.

Our present paper contains the results obtained at  $445^\circ$ . This communication appears to us to be of importance for the following reasons. Three months after our first paper a communication appeared from SCHENCK and ZIMMERMANN<sup>2)</sup> from which it appeared that they had also studied the transformation of CO into  $\text{CO}_2$  and C and had arrived at the result that the reaction at temperatures from  $310^\circ$  and  $360^\circ$  was a unimolecular one, thus confirming our experiments, but that at  $445^\circ$  the reaction became bimolecular.

On continuing our investigation we found, however, that the

<sup>1)</sup> Proc. 8 Jan. 1903.

<sup>2)</sup> Ber. 36. p. 1231.

reaction at  $445^\circ$  is also a unimolecular one and that therefore the observations of SCHENCK and ZIMMERMANN must be faulty as far as the temperature  $445^\circ$  is concerned.

### Experiment.

In order that the reaction might not take place too rapidly the reaction vessel was now filled one third with the catalyser (pumice-nickel-carbon)<sup>1)</sup>.

The object of the first experiments was to determine the order of the reaction according to the method of VAN 'T HOFF.

In the first measurement the initial pressure was 770.7 m.m. Hg. After 5 minutes the CO tension amounted to 430.5 m.m. Hg from which

$$\frac{dc_1}{dt} = 68,04$$

and for the average pressure of the carbonic oxide

$$c_1 = 600,6$$

In the second measurement the initial pressure was 442.2 m.m. Hg and after 5 minutes the CO pressure amounted to 239.0 m.m. Hg.

Here  $\frac{dc_2}{dt} = 40,64$  and  $c_2 = 340,6$ .

If from this we calculate  $n$  according to the formula of VAN 'T HOFF

$$n = \frac{\log \left( \frac{dc_1}{dt} : \frac{dc_2}{dt} \right)}{\log (c_1 : c_2)},$$

we obtain

$$n = 0,91. ^2)$$

2. After having thus become convinced that the reaction at  $445^\circ$  is also a unimolecular one we made a series of measurements in order to calculate the reaction constant from them.

The result was as follows:

<sup>1)</sup> The quantity of iron present in pumice did not appear to exert any influence as no alteration in pressure was noticed in a reaction vessel containing pumice and CO when heated to  $445^\circ$ . This time, however, as in SCHENCK's experiments, the iron was removed from the pumice by reduction with hydrogen and subsequent treatment with HCl and boiling in a Soxhlet apparatus.

The  $\text{Ni}(\text{NO}_3)_2$  originally contained much iron, but was completely freed from it by leaving the solution for some time in contact with  $\text{NiCO}_3$ .

<sup>2)</sup> Also after a longer time (10—15 minutes)  $n$  was found to be practically 1.

Time in minutes.	Pressure in m.m. Hg.	$k = \frac{1}{t} \log \frac{P_0}{2 P_t - P_0}$	$k' = \frac{1}{t} \frac{2(P_0 - P_t)}{P_0(2 P_t - P_0)}$ <sup>1)</sup>
0	769.5		
4	660.1	0.03437	0.000129
6	616.6	0.03666	0.000143
8	579.1	0.03707	0.000159
10	548.7	0.03704	0.000175
15	497.8	0.03546	0.000208
20	476.7	0.03108	0.000206
30	466.3	0.02246	0.000161

The measurement was started here half a minute after the commencement of the filling. The filling lasted  $\frac{1}{4}$  minute.

The third column contains the values of  $k$  calculated on the supposition that the reaction is *unimolecular* whilst the fourth column contains the values of  $k'$  assuming the reaction to be *bimolecular*, as believed by SCHENCK and ZIMMERMANN. In concordance with what has been found above, we see that the figures in the third column are much more nearly constant than those in the fourth. During the first 15 minutes the values of  $k$  (third column) agree fairly well with each other; afterwards a slow fall takes place. That the first constant would be smaller than the next was to be expected, as during the first 4 minutes a small expansion had still to take place.

Although the starting point could not be fixed with the same accuracy as before, owing to the greater velocity of the reaction, the fall of  $k$  could not be attributed to experimental errors. It therefore, made us suspect that the reaction might perhaps prove to be perceptibly reversible at 445°.

It is true that BOUDOUARD<sup>2)</sup> had found that CO when in contact with our catalyser was completely decomposed at 445° into CO<sub>2</sub> and C, but as his method was not very accurate we felt we might doubt this result<sup>3)</sup>.

In order to obtain certainty we made the following experiment. We filled the apparatus at 445° with CO<sub>2</sub> and observed whether an

<sup>1)</sup> SCHENCK and ZIMMERMANN have made a mistake calculating the value of  $k'$ .

<sup>2)</sup> Ann. de Chim. et de Phys. [7] T. 24. Sept. p. 5—85 (1901).

<sup>3)</sup> SABATIER and SENDERENS noticed a complete transformation between 230° and 400°. Bull. Soc. Chim. t. 29 p. 294 (1903).

increase of pressure took place which would indicate that the reaction  $\text{CO}_2 + \text{C} = 2 \text{CO}$  was proceeding.

The experiment removed all doubt as not only an increase of pressure be could very plainly demonstrated, amounting after a few hours to several c.m. of mercury, but after exhausting the apparatus a quantity of CO could be detected in the gaseous mixture which accounted for the observed increase of pressure.

Contrary to BOUDOUARD's results we have therefore found that the reaction  $2 \text{CO} = \text{CO}_2 + \text{C}$  is *reversible* at  $445^\circ$ .

The reason why fairly concordant constants were obtained during the first 15 minutes although no notice had been taken in the calculation of the reversal of the reaction, is simply that the equation

$$\frac{dx}{dt} = k_1(A-x) - k_2 \frac{x}{2} \quad \dots \quad (1)$$

differs but very little from

$$\frac{dx}{dt} = k_1(A-x) \quad \dots \quad (2)$$

when  $k$  or  $x$  or both are very small.  $k_2$  is very small at  $445^\circ$  and this is the reason why at first the second equation is satisfied,  $x$  being then not yet large.

By means of the first equation we might be able to calculate  $k$  if we knew the equilibrium constant  $K = \frac{k_1}{k_2}$ .

As analysis seemed to us less accurate we have endeavoured to determine  $K$  in the following manner:

The reaction vessel was filled again with CO, while the time was noted which elapsed between the filling and the first reading so as to be able to find the starting pressure by extrapolation. The heating at  $445^\circ$  was now continued until the pressure after the lapse of some hours did not undergo any further change.

$K$  could then be calculated from the pressure at the start and at the finish.

To decide whether the final pressure corresponded with a real condition of equilibrium, the same experiment was repeated starting with  $\text{CO}_2$ . If the first final condition had been a real equilibrium, the same value ought now to be found for  $K$ .

Up to the present we found this by no means to be the case but we do not at all consider the research finished in this direction. We

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1) It is taken for granted here that the reaction  $\text{CO}_2 + \text{C} = 2 \text{CO}$  is also a unimolecular one.

only mention it to explain why the values for  $k$  in our last table have not been corrected.

3. In criticising the experiments of SCHENCK and ZIMMERMANN, it must first of all be observed that they did not reduce their NiO with CO but with H<sub>2</sub>. This is of course, wrong as during the reaction carbon is deposited and the catalytic Ni surface is changed. If, as in our experiments, we start with Ni on which previously a coating of carbon has deposited, it is evident that a further precipitation of carbon during the experiment will be of less consequence.

In our former communication it has moreover been shown that the activity of the catalyser first diminishes owing to deposition of carbon, but finally becomes practically constant.

If, therefore, we start with Ni without carbon we may expect that, on account of the deposition of carbon,  $k$  will continuously decrease. The values for  $k$  found by SCHENCK and ZIMMERMANN are not at all constants and show a decrease with an increase of the time.

To find out what can be the cause of the *bimolecular* course at 445° as found by SCHENCK and ZIMMERMANN we have repeated the experiment with pumice-nickel in which the NiO had been reduced with very pure hydrogen. <sup>1)</sup>

Our first work was again the determination of the order of the reaction.

$$\begin{array}{ll}
 \text{1st measurement.} & \text{Initial pressure} = 756,0 \text{ m.m. Hg} \\
 & \text{CO pressure after 3 min.} = 528,6 \quad \text{''} \quad \text{''} \\
 & \frac{dc_1}{dt} = 75,8 \quad c_1 = 642,3
 \end{array}$$

$$\begin{array}{ll}
 \text{2nd measurement.} & \text{Initial pressure} = 275,1 \text{ m.m. Hg} \\
 & \text{CO pressure after 2 min.} = 210,9 \quad \text{''} \quad \text{''} \\
 & \frac{dc_2}{dt} = 32,1 \quad c_2 = 243,0 \\
 & \text{therefore} \quad \quad \quad n = 0,9 \text{ } ^2).
 \end{array}$$

Having found that, contrary to the statement of SCHENCK and ZIMMERMANN, the reaction with this catalyser is also *unimolecular* we made a further series of measurements in order to calculate  $k$ .

The results were as follows:

<sup>1)</sup> By electrolysis of a NaOH solution, using nickel electrodes.

<sup>2)</sup> After a longer time (5–10 minutes)  $n$  was found to be practically 1.

Time in minutes.	Pressure in m.m. Hg.	$k = \frac{1}{t} \log \frac{P_0}{2 P_t - P_0}$
0	762.4	
2	671.7	0.05830
4	606.3	0.05708
6	560.5	0.05451
8	528.8	0.05143
10	508.6	0.04753

The larger values of  $k$  and their regular change are due to the absence of a layer of carbon at the commencement of the experiment.

If we compare this table with the one given by SCHENCK and ZIMMERMANN for 445°

Time in minutes.	Pressure in m.m. Hg.	$k = \frac{1}{t} \log \frac{P_0}{2 P_t - P_0}$
0	759	
2	626	0.09369
4	548	0.08815
6	522	0.07090
10	510	0.04636

we notice that the very considerable change of  $k$  cannot be fully explained by the absence of a layer of carbon but that there must have been another disturbing factor.

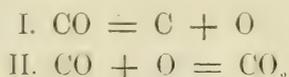
From SCHENCK and ZIMMERMANN's description it is evident that it cannot be the absorbed hydrogen<sup>1)</sup>, for this was introduced into their apparatus only in the *first* series of experiments and the second series shows a still greater change.

For want of further particulars as to the research of SCHENCK and ZIMMERMANN we cannot make any further suggestions as to the nature of this second disturbing factor.

<sup>1)</sup> We found that H<sub>2</sub> is very strongly absorbed by finely divided Ni but gradually expelled in vacuum. According to SABATIER and SENDRENS [C.r. 134 p. 514—516 (1902)] CO and H<sub>2</sub> react with each other above 200° in contact with finely divided nickel according the equation: CO + 3 H<sub>2</sub> = CH<sub>4</sub> + H<sub>2</sub>O.

We must say a few words about their plausible explanation of the change from a *unimolecular* to a *bimolecular* course, which they thought they had discovered.

After having made the same supposition as we did for the unimolecular course namely



they say:

„Der Dissociation des Kohlenoxydes in seine Elemente würde dann ein Oxydationsvorgang folgen. Spielt sich der letztere, wie bei dem Sauerstoff im status nasens zu erwarten ist, mit sehr grosser Geschwindigkeit ab, welche die Dissociationsgeschwindigkeit übertrifft, so findet man eine monomolekulare Reaction. Steigt bei höherer Temperatur die Geschwindigkeit des Dissociationsvorganges verhältnissmässig mehr an als die des Oxydationsprocesses, so fallen schliesslich die Vorgänge zeitlich zusammen, und wir erhalten den Eindruck einer bimolecularen „gekoppelten“ Reaction.

Auf diese Weise lässt sich für die auffällige Erscheinung eine plausible Erklärung geben.“

But what has been overlooked here is that in order that the reactions I and II shall give the impression of a unimolecular reaction, the second must take place with immeasurable velocity. If this is true at a low temperature it is certainly so at higher temperatures and even if the velocity of the first reaction has increased this will be the only one which will be observed so long as it proceeds with measurable velocity.

We are, therefore, inclined to contend that it is plausible to assume that if the reaction is a unimolecular one at a low temperature it cannot be expected that the order of the reaction will increase at a higher temperature.

Summary of our conclusions:

1. The transformation of CO into CO<sub>2</sub> and C is unimolecular for all the temperatures at which we have experimented: 256°, 310°, 340° and 445°.

2. Contrary to the result obtained by BOUDOUARD the reaction is reversible at 445°.

3. The equilibrium constant could not be determined, as up to the present, we have found that the same condition of equilibrium is not attained starting from CO and from CO<sub>2</sub> + C.

Amsterdam, Chem. Lab. University, May 1903.

**Physiology.** — “*A new law concerning the relation between stimulus and effect.*” By Prof. J. K. A. WERTHEIM SALOMONSON (6<sup>th</sup> Communication). (Communicated by Prof. C. WINKLER).

(Communicated in the meeting of May 30, 1903)

The numbers used for testing our law concerning the relation of stimulus and effect, were for the greater part derived from lifting-heights in cases of *isotonical* muscle-contractions. During each contraction the tension of the muscle is not perceptibly altered, likewise the tension remained the same for all contractions belonging to each single series.

What is the influence of any change of weight on the magnitude of the constants? It is known already that the lifting-height changes whenever the tension is changed in any manner. In the formula, expressing the law for the relation between stimulus and effect

$$E = A \{ 1 - E^{-B(R-c)} \}$$

the maximum lifting-height is represented by the constant  $A$ . As the lifting-height denotes at the same time the maximum quantity of external labour, we may state directly that the constant  $A$  will certainly be changed at any alteration in the magnitude of weight.

As a matter of course nothing is known about the constant  $B$ , neither could I find any indication about the constant  $C$ , representing the threshold-value of the stimulus. It is thence of some importance to investigate what will happen to the constants  $B$  and  $C$ , if we alter the weight attached to the muscle.

To this purpose I have recorded a series of isotonical contractions of frog-muscles at increasing stimulus. I generally used a gastrocnemius-preparation, which was stimulated by means of the nerve. The experiments were made indifferently with muscles cut out or with muscles through which the blood circulated in the normal manner, these offering not the slightest difference between them.

The stimulus employed, was the current of charge of a condensator of 0.001 microfarad. This was done by pushing down a morsekey mounted on ebonite, thus connecting the condensator with two points between which there existed a known potential difference; in so doing the current of charge of the condensator was led through the nerve of the preparation. When letting go the key the condensator was short-circuited and discharged. The variable difference of tension was obtained by means of a rheochord with platinum-iridium wire, calibrated with the utmost care, through which a constant current was sent by a large accumulator. By means of a variable steadying resistance care was taken that the P. D. at the ends of the wire, measuring one meter,

amounted to exactly 1 Volt. This P. D. was continually controlled by a recently calibrated precision-galvanometer of SIEMENS and HALSKE. In this way every millimeter of the wire represented 0.001 Volt. By means of a vernier 0.1 millimeter could be read without difficulty. Ever millimeter represented in this manner at the same time one millionth part of a microcoulomb. The shocks of the current followed one another with intervals of 15 seconds.

I have succeeded, not without some trouble, in obtaining two complete series, one of which I have entirely calculated and inserted here. It consists of five separate series, each including from eight to ten contractions, all taken from the same gastrocnemius, but in each succeeding series the weight was increased.

## Series I. Weight 10 Gr.

<i>R</i>	<i>A</i> = 19.15 <i>E<sub>calc.</sub></i>	<i>B</i> = 0.0204 <i>E<sub>meas.</sub></i>	<i>C</i> = 356.3 <i>f</i>
375	6.073	6.1	+ 0.027
400	11.297	11.0	- 0.297
425	14.435	14.4	- 0.035
450	16.318	16.6	+ 0.282
475	17.450	17.2	- .250
500	18.429	18.0	- 0.429
525	18.537	18.5	- 0.037
550	18.782	19.0	+ 0.218
600	19.017	19.1	+ 0.083
650	19.102	19.2	+ 0.098

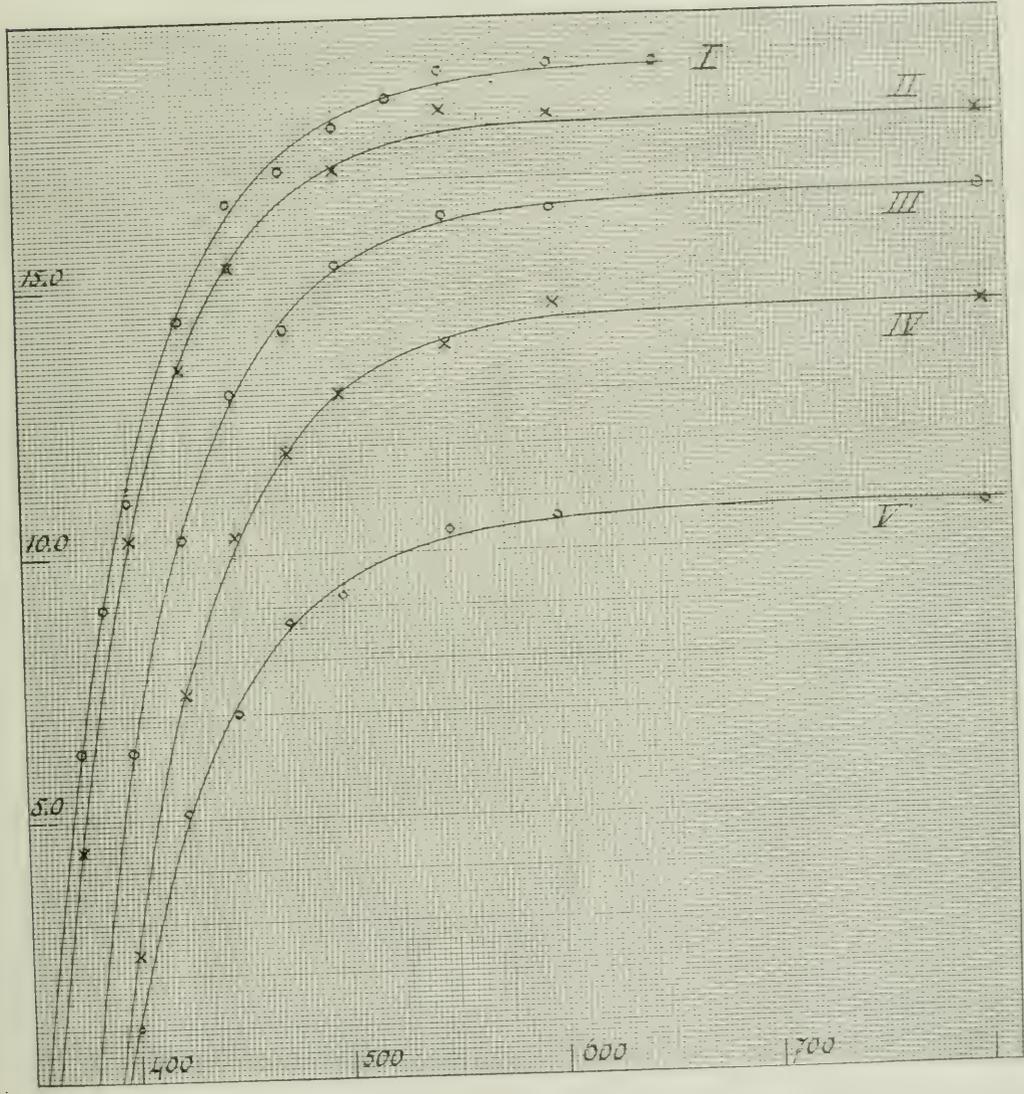
Consequently the mean observation error of each single observation amounts to:

$$\sqrt{\frac{\sum \sigma^2}{n-3}} = 0.2102.$$

## Series II. Weight 30 Gr.

<i>R</i>	<i>A</i> = 18.21 <i>E<sub>calc.</sub></i>	<i>B</i> = 0.0213 <i>E<sub>meas.</sub></i>	<i>C</i> = 361.6 <i>f</i>
375	4.521	4.4	- 0.121
400	10.173	10.2	+ 0.027
425	13.491	13.5	+ 0.009
450	15.439	15.4	- 0.039
500	17.255	17.2	- 0.055
[550	17.883	18.3	+ 0.417]
600	18.097	18.2	- 0.103
800	18.206	18.2	- 0.006

J. K. A. WERTHEIM SALOMONSON. "A new law concerning the relation between stimulus and effect."





The mean observation error amounts to 0,0876, if we neglect the observation placed in parenthesis, which was not used for the calculation.

## Series III. Weight 60 Gr.

$$A = 16.68 \quad B = 0.0202 \quad C = 377.0$$

<i>R</i>	<i>E<sub>calc.</sub></i>	<i>E<sub>meas.</sub></i>	<i>ρ</i>
400	6.199	6.3	+ 0.101
425	10.359	10.3	- 0.059
450	12.863	13.0	+ 0.137
475	14.376	14.2	- 0.176
500	15.290	15.4	+ 0.110
550	16.174	16.3	+ 0.126
600	16.496	16.4	- 0.096
800	16.674	16.6	- 0.074

The mean observation error amounts to : 0.1457.

## Series IV. Weight 100 Gr.

$$A = 14.52 \quad B = 0.0209 \quad C = 391.0$$

<i>R</i>	<i>E<sub>calc.</sub></i>	<i>E<sub>meas.</sub></i>	<i>ρ</i>
400	2.490	2.4	- 0.090
425	7.386	7.4	+ 0.014
450	10.055	10.3	+ 0.245
475	12.011	11.9	- 0.111
500	13.032	13.0	- 0.032
550	13.997	13.9	- 0.097
600	14.336	14.6	+ 0.264
800	14.492	14.5	+ 0.008

The mean error amounts to : 0.1793.

## Series V. Weight 160 Gr.

$$A = 10.74 \quad B = 0.0198 \quad C = 394.4$$

<i>R</i>	<i>E<sub>calc.</sub></i>	<i>E<sub>meas.</sub></i>	<i>ρ</i>
400	1.127	1.0	- 0.127
425	4.880	5.1	+ 0.220
450	7.168	7.0	- 0.168
475	8.563	8.7	+ 0.137
500	9.413	9.2	- 0.213
550	10.247	10.4	+ 0.153
600	10.557	10.6	+ 0.043
800	10.737	10.7	- 0.037

The mean error amounts to: 0.1916.

These series may teach us in the first place that no change whatever in the general course of the curve is effected by the magnitude of weight. The constants only are altered. The following table will give an easier survey of the manner in which these changes are effected. The weight is therein represented by  $L$ , whilst  $A$ ,  $B$  and  $C$  stand for the three constants of our formula; in the third column under  $ALV$  is given in gram-millimeters the amount of work done multiplied by the writing-lever. This enlargement, which in our case took place in the ratio of 5 : 1 will be denoted by  $V$ .

$L$	$A$	$ALV$	$B$	$C$
40	49.45	491.5	0.0204	356.3
30	48.21	546.3	0.0213	361.6
60	46.68	1000.8	0.0202	377.0
100	44.52	1452.	0.0209	391.0
160	40.74	1718.4	0.0198	394.4

In this table we may observe:

1<sup>st</sup>. That at increment of weight the lifting-height diminishes, at first slowly, afterwards more rapidly, an already well-known fact.

2<sup>nd</sup>. That the work done increases at first rapidly, afterwards more slowly. As we know, the work would, if the weight were still further increased, attain at last a maximum value and finally diminish.

3<sup>rd</sup>. That to all practical purposes *the coefficient B remains constant with increasing weight*. For its mean value amounts to 0.02052, the largest deviation being at the utmost 3.8 ‰, the most probable value being:  $0.02052 \pm 0.000395$ . Furthermore the deviations are irregular in both directions, so we may conclude that under ideal technical conditions the increment-constant would have remained, to all probability, wholly unaltered by different weights.

4<sup>th</sup>. That the constant  $C$ , i.e. *the minimum threshold-value augments at increment of weight*. I did not yet find this fact mentioned in the literature within my reach. Still it may be easily verified even without writing the record of a complete series, and it was proved beyond any doubt within the limits of the experiment.

With regard to the series here communicated, we ought to make mention of the fact that still another series was written, the weight therein being 200 Gr.; this last series however showed technical faults of too much importance, than that it could be employed for the calculation of the constants.

Besides the experiments on isotonical contractions with different weights, I also investigated isometrical contractions. I believe that the

communication of two of these series will suffice. The first was taken from the second gastrocnemius of the same frog that had supplied us with the preparation of the foregoing series.

## Series VI. Isometrical.

$R$	$A = 10.8$ $E_{calc.}$	$B = 0.0231$ $E_{meas.}$	$C = 384.0$ $f$
400	3.163	3.2	+ 0.037
425	6.611	6.4	- 0.211
450	8.449	8.4	- 0.049
475	9.480	9.7	+ 0.220
500	10.059	9.9	- 0.159
550	10.567	10.7	+ 0.133
600	10.726	10.7	- 0.026
800	10.800	10.8	0.000

$$\varrho = 0.1675,$$

## Series VII. Isometrical.

$R$	$A = 12.22$ $E_{calc.}$	$B = 0.0096$ $E_{meas.}$	$C = 487.0$ $f$
500	1.433	1.6	+ 0.117
550	5.546	5.5	- 0.046
600	8.091	8.3	+ 0.209
650	9.666	9.9	+ 0.234
700	10.639	10.2	- 0.439
750	11.242	11.1	- 0.141
800	11.615	11.6	- 0.015
850	11.846	11.9	+ 0.054
900	11.989	12.0	+ 0.011
950	12.077	12.0	- 0.077

The mean observation-error amounts to:  $\varrho = 0.2190$ .

Here again there is sufficient accordance to leave no room for doubt.

Meanwhile it is of importance to remark that both the coefficient  $A$  and the effect  $E$  have in this series quite another signification as they did in cases of isotonical contractions.

Here the maximum tension attained by a muscle during the contraction, is measured by  $E$ , whilst the highest tension, attainable

for that muscle during any single twitch is indicated by *A*. And in this case again it is shown that our law concerning the relation between stimulus and effect enables us to represent with sufficient accuracy the increment of effect whenever the stimulus is increased. At present we only wish to state this fact without entering into any details about its theoretical significance for our knowledge of the course of isometrical contractions.

**Meteorology.** — At the chairman's proposal it was resolved to insert in the Proceedings the following *Extract from the Report made in the extraordinary meeting held this day by the committee for awarding the BUYS-BALLOT Medal, consisting of Messrs. JULIUS, HAGA, ZEEMAN, VAN DER STOK and WIND.*

In the meteorological literature of late years one definite line of development in this science has come to the front in such a degree that, in the opinion of the committee, it is obvious to award the BUYS-BALLOT Medal for this time to a representative of this peculiar branch of meteorological investigation.

The branch referred to is one of mainly experimental investigation.

In the opinion of some the material collected by the meteorologists during a long series of years grows so dangerously extensive that, for instance, Professor SCHUSTER could not help in the last meeting of the British Association expressing a wish, that the meteorologists might stop their observations for some five years and during that time might unanimously try to assimilate the materials in store and to compose a reasonable programme. SCHUSTER in expressing a wish, as to stopping the observations, cannot have been in full earnest, as he will grant too that the series of observations, partly as material for climatic studies, partly as a basis and a test for future theories have a permanent value and should not be rashly interrupted. Nevertheless it is true that, in order to prevent waste of capital and labour and to avoid the loss of valuable data, it is very desirable, in continuing former series of observations, to constantly keep in view their value and not to plan others but on reasonable grounds.

Yet, rather a short time ago the material referred to above, however extensive, showed an important deficit. Most obviously it did so, when considered as the foundation of a theory about the great problems of meteorology, the general circulation of the atmos-

phere and the nature of cyclones. When leaving out of consideration the mountain-stations, whose importance for the purpose in question is rather limited, the facts observed referred on the whole to the lower layers of air. This is the reason, why opinions about the movement of the air in its higher layers, and therefore about the entire mechanism of circulation, opinions long ago defended by DOVE, MAURY, FERREL, JAMES THOMSON &c. on the ground of their more or less incomplete theories, could hold their own by the side of each other, though in some respects not in keeping with each other. For the same cause incorrect ideas about the distribution of temperature in the atmosphere, closely connected with the circulation, could remain in existence, and important inferences respecting this distribution, derived from theoretical considerations — the Committee are in the first place thinking of the interesting thermodynamic investigations of VON BEZOLD — could not yet be put to the test by direct observations.

As an extremely important step in the right direction, therefore, may be considered the extension of the meteorological investigations to higher layers of the atmosphere. And so much the more, with a view to the remark made in connection with Prof. SCHUSTER's opinion, should this step be applauded, because it was taken with the utmost care and with a sharply outlined purpose. This investigation, entered upon in a former decennary, has in the last ten years been systematically set about and organized in an efficient way.

If there were one investigator, who could be considered as the only proper founder and promoter of this new branch of meteorological investigation, the Committee would not hesitate to design him for the BUYS-BALLOT Medal. This, however, being not the case, but there being many explorers, who in the higher ranks have contributed to its development, it seems advisable to award the medal to him among so many, who distinguished himself most by his work. Here, again, it was not easy to choose, the conditions, under which the labour was done, showing large differences and a decisive rate of comparison being wanting.

On one side the attention was immediately drawn to A. LAWRENCE ROTCH, the energetic director of Blue-Hill Observatory, founded and maintained through private means. He was the first to make use, on a large scale and systematically, of kites, provided with registering instruments, to become acquainted with the values of meteorological elements several kilometers high in the air and to put beyond all doubt the practical usefulness and appropriateness of this method. Moreover he set the example of using steamships in the observations with kites, to overcome the difficulty of too great or too slight a force

of the wind, and finally planned an expedition with a purpose of trying by experiment with kites on board a steamship to make sure about the movement of the air above the regions of the trade-winds.

Another investigator, working under similar conditions with no less skill and success, is L. TEISSERENC DE BORT, the founder and proprietor of the "Observatoire de Météorologie Dynamique" at Trappes. Having been already for a long time organising ascents for meteorological purposes this excellent investigator in later years started his "ballons-sonde" in France and in foreign countries in large numbers, to record temperature and moisture of the atmosphere at a height of 10 to 15 kilometers. In the meanwhile he was indefatigably working at the improvement of the recording-apparatus. Now, for nearly a year, he is — supported by the Swedish and Danish Governments — very successfully engaged in a systematic examination, by means of kites and balloons, of the atmosphere above Jutland and the Danish Isles.

On the other side much respect and admiration are due to the perseverance and talent, with which H. H. HILDEBRANDSSON since 1873 has been trying by means of a large system of stations to make simultaneous observations of clouds and to get from these the knowledge of the movements of the upper air, necessary for a development of the theory of general circulation. He began with observations in Sweden, but knew by pointing to first results of obvious importance how to rouse gradually interest for the labour with the meteorologists of nearly all nations, especially with the "International Meteorological Committee." This led to the nomination of an international committee for the observation of clouds and in consequence to the publication of an international cloud-atlas, in which it was principally his nomenclature of the different forms of clouds that was adopted and elucidated by plain illustrations. Finally it led also to the issuing of simultaneous observations all over the civilised world during a whole year, the "cloud-year" 1896/97.

Very important are the results which have been derived by HILDEBRANDSSON from the materials gathered. Some current ideas about the movements of the upper air seem to be entirely subverted. They have shown e. g. that in the (northern) temperate zone both the upper and the lower air on an average perform a whirling movement in the sense of the earth's rotation, round the pole as a centre, but with a centripetal component in the lower, a centrifugal component in the higher layers, a movement, therefore quite different, from the south-western lower current and the north-western higher

current, almost generally adopted hitherto. Of the Report about the cloud-year only a first part has yet appeared.

Mention must also be made of Professor H. HERGESELL, the impulsive and able chairman of the International aeronautic Committee. In this quality he has contributed much to promote a systematic examination of the higher air and has taken the initiative for the simultaneous international ascents of balloons, which since November 1900 are being undertaken on the first Thursday of each month from some ten stations. Moreover he has by his own investigations very successfully contributed to the common task.

Though it would be easy to mention some more meteorologists, to whom the new branch of investigation owes nearly equally much, it seems to be difficult, after all these men of great merits, to indicate another who should more than one of them have advanced Meteorology by his labour in the line considered. Accordingly the Committee do not intend to name one person, but wish to recommend for the Medal two investigators — who are, however, one in their work — viz, the editors of “Die Wissenschaftlichen Luftfahrten des deutschen Vereins zur Förderung der Luftschiffahrt, in Berlin”, RICHARD ASSMANN and ARTHUR BERSON.

The reason which has determined the Committee to hold these two explorers as more than any one else worthy of the distinction, is especially the high value of the said publication. There the editors have laid down the foundations, the course and the results of their highly important series of investigations, at the same time clearly showing their great perseverance and earnestness in their exertions, their great scrupulousness and punctuality in the accomplishment of their task. This publication, in which moreover numerous new instruments and resources are described and results communicated which immediately have appeared to be of great value, is undoubtedly a work of classic importance.

The balloon-expeditions, described in this work, were made from 1888 to 1899 and are divided into 6 preparatory (1888—1891), 40 principal (1893—94) and 29 supplementary expeditions; besides experiments were made with a registering captive balloon and with registering free balloons. In reality the scientific aerial voyages, made at Berlin, have not been finished herewith. Among those not described in the work we mention the rightly well-known “Hochfahrt” of BERSON and SÜRING, undertaken especially to verify the instruments of the registering free balloons by comparing their records with eye-observations made in a manned balloon started at the same time. The free balloons being meant for the greatest heights

(twenty kilometers and more), the manned balloon, in which the parallel observations were made, had to rise as high as possible. It was planned to go as high as ten kilometers and reached even a height of nearly eleven.

It is easy to see that expeditions to such a height cannot be free from danger, if we think of the atmospheric pressure of  $\pm 200$  mM and of the temperature to below  $-40^{\circ}\text{C}$ ., which have been observed at these heights. The homage then, which the committee wish to be paid to BERSON, applies partly to the courage and the intrepidity, with which this explorer has frequently risked his life in behalf of the uncommon task, which he imposed upon himself in the service of science.

The whole work, published in 1899/1900, consists of three big quarto volumes. The first of these is partly devoted to an historical and critical survey of the development of scientific aerial voyages, partly also it deals with the construction of balloons and instruments and with the methods of observation and reduction. Moreover it contains the data as to the tracks covered by the balloons and the figures got by the observations. The second volume offers an ample description of the separate aerial voyages. In the third the observations are sifted and discussed, being treated under different heads as: temperature of the air, moisture, formation of clouds, velocity of wind, direction of wind, radiation, atmospheric electricity. This volume winds up with a chapter, written by VON BEZOLD, and entitled: "Theoretische Schlussbetrachtungen".

Here we should not omit mentioning the names of BASCHIN, BÖRNSTEIN, GROSS, KREMSER, STADE and SÜRING, who have all of them contributed to the composition of the great work and also personally taken part in the scientific aerial voyages.

A short survey of the provisional results of a more general tenor must not be left aside here.

1<sup>st</sup>. Formerly it has sometimes been thought that the temperature in the higher layers of the atmosphere approached a limit of  $-35$  to  $-50^{\circ}\text{C}$ .; these investigations however do not at all point to the existence of such a limit. Temperatures also, considerably lower than the above, have come to light.

2<sup>nd</sup>. In the lower layers of the atmosphere the temperature, in rising, diminishes on the whole less rapidly than would answer to convective equilibrium. Above 4000 M, however, the rate of decrease grows larger and seems to approach that value of nearly  $1^{\circ}\text{C}$ . per 100 meters as a limit. This is in keeping with a supposition of VON BEZOLD based on theoretical grounds, whilst the behaviour in lower

layers can be accounted for by the influence of radiation, condensation and evaporation.

The distribution of temperature found in this way, is satisfactorily in agreement with the one found by TEISSERENC DE BORT, but disagrees considerably with that which was formerly determined by GLAISHER.

3<sup>rd</sup>. The diurnal variation of temperature has at a height of 2500 M. shrunk down to less than  $\frac{1}{10}$  of its amplitude at the surface of the earth.

Of the annual variation of temperature the amplitude decreases rapidly in the lowest layer of 500 M. Higher on it is rather a retardation of the maximum and minimum of temperature than a decrease of amplitude, which is still obvious. At a height of 4000 M the highest and lowest temperatures seem to occur about the middle of September and March.

The non-periodical changes of temperature in the higher layers are hardly less intensive than at the surface of the earth.

4<sup>th</sup>. Frequently low, but also sometimes higher in the atmosphere, there are layers in which the temperature increases instead of decreasing with the height. "Inversions" to an amount of even 16°C. have been observed.

Not seldom there are also layers, in which the temperature in rising diminishes more rapidly than would answer to the convective equilibrium. It is very remarkable that these layers, which obviously tend to provoke a state of unstability in the atmosphere, are often of a great thickness, reaching even 2500 meter, for instance.

5<sup>th</sup>. In accordance with results which HANN came to in the Alps, it has appeared that above Middle-Europe, both in winter and in summer, the temperatures at equal heights in anticyclones are in general higher than in cyclones — this, at least, holding good for heights up to 8 KM. This result tends to corroborate the conviction of most meteorologists that the cyclones with their ascending and the anti-cyclones with their descending currents of air cannot as a rule simply owe their existence to differences of temperature. By still more recent investigations it has appeared that the rate of decrease of temperature above the anticyclones, though at first smaller, is at greater heights greater than the above cyclones, so that it remains possible that in the very high layers of the atmosphere the temperature above the anticyclones is lower than above the cyclones.

6<sup>th</sup>. In most of the cases several layers of a quite different nature and origin were clearly indicated in the atmosphere.

7<sup>th</sup>. In rising, the moisture of the atmosphere generally decreases

more than HANN had derived from observations of mountain-stations and from those made by GLAISHER.

8<sup>th</sup>. Important data have been acquired about the formation and origin of clouds, in connection with the distribution of the meteorological elements.

9<sup>th</sup>. The velocity of wind increases with the height, strongly in the layers below 1000 and above 3000 M, less so between these two heights. At a height of 5000 M it was on an average 4.5 times as large as at the surface of the earth. Important data were also acquired about the difference in the direction of the wind between the lower and higher parts of the atmosphere.

10<sup>th</sup>. Thermally and electrically the surface of a layer of clouds has a similar effect upon the region above it as the surface of the earth.

11<sup>th</sup>. The rate of decrease of electrical potential seems to diminish, when rising, and even to vanish entirely in the higher regions of the atmosphere. This result, arrived at from only few observations, has afterwards been corroborated.

It is not only the initiative in and the organisation, guidance, partly also execution of, this interesting investigation, which are mainly due to ASSMANN. We also owe to him the construction of the aspiration-thermometer and -psychrometer, which has first rendered possible trustworthy observations as to temperature and moisture under the most different circumstances. It has appeared that in former balloon-expeditions (of GLAISHER e.g.) errors to the extent of even 15°, owing to radiation, must have occurred in the indications of the thermometers.

Finally we ought to mention the introduction by ASSMANN of the highly appropriate "Platz"-balloons made of caoutchouc, which as free registering-balloons can reach even a height of 20 to 30 kilometers; there they burst and, provided with a parachute, return to the earth very slowly with the instrument they convey.

What is said above may be a sufficient reason for awarding the medal to ASSMANN and BERSON; yet the committee cannot omit referring to the excellent work which is being done in the aeronautic observatory at Tegel near Berlin, founded by ASSMANN in 1899 and being directed by him. Here daily observations are made for the examination of the upper air with the aid of kites, kite- and Platz-balloons. The results are published daily and, since the beginning of this year, as graphic reviews also monthly.

If an examination of the higher layers of air can furnish many important data more for our insight into the mechanism of atmospheric phenomena — which is hardly to be doubted — such a

systematic train of working as is adopted at Tegel seems above all things to be conducive to that purpose, especially if the example given there be followed in a sufficient number of stations elsewhere.

In the Tegel observatory BERSON as "ständiger Mitarbeiter" is steadily cooperating with its director.

One of the more recent results, arrived at in the Tegel observatory, may still be mentioned here. In the spring of 1902 registering balloons recorded between 12 and 16 kilometers an inversion of temperature to an amount of 9°. This seems to point to an equatorial current in those parts of the atmosphere which, even higher than the region of the cirrus-clouds, could not but escape HILDEBRANDSSON's observations.

Almost simultaneously an inversion was observed above France by TEISSERENC DE BORT at a height of more than 10 kilometer.

The above will certainly be sufficient to give an idea of the nature and the importance of the new field and the new methods of investigation and to convince you that the development of these methods owes very much indeed to the two investigators, to whom we last drew attention.

Concluding the Committee beg to report that in their unanimous opinion the BUYS-BALLOT Medal should be awarded to RICHARD ASSMANN, Director of the Aeronautic Observatory at Tegel, and ARTHUR BERSON, permanent collaborator to the same institution, as a homage to the great services they have rendered to the development of Meteorology, not only in their just mentioned qualities, but also and especially as editors of the work entitled: "Die Wissenschaftlichen Luftfahrten des deutschen Vereins zur Förderung der Luftschiffahrt", and as those who have had the greatest share in the investigations described in this principal work.

**Botany.** — "*On a Sclerotinia hitherto unknown and injurious to the Cultivation of Tobacco*" (*Sclerotinia Nicotianae* OUD. et KONING). (Postscript). By Prof. C. A. J. A. OUDEMANS and C. J. KONING.

With regard to the small dimensions of the cups (apothecia) of *Sclerotinia Nicotianae*, as sketched in our essay (breadth 0,8, depth 0,2 millimetres) we think it worth while to point out that much stouter cups were obtained from sclerotia which on the 9<sup>th</sup> of March ult. were sown out afresh in the known manner in different

kinds of earth (forest-humus, garden-earth, sand, pounded autumn-leaves of *Quercus* and *Fagus*).

After the experimental dishes, covered with glass, had been placed on a windowsill outside and for 8 weeks had shown no sign of life, stemmed cups were found on the sclerotia in all of them, differing from those obtained formerly in having greater dimensions. Instead of 0.8 mill. wide and 0.2 deep, the cups were now 1.4—5 mill. wide and 0.2—0.3 mill. deep; the stems on the other hand were much shorter, varying between 1.5 and 9 mill. against 4—6 cent. in March.

The new numbers agree more with those of other species of *Sclerotinia* and can only, we think, have been produced by the influence of a milder temperature and corresponding increased metabolism.

The greatest number of cups, sprung from one sclerotium, was 12, as may be seen in the illustration.

The special features of cups and stems, among which the swelling under the cups, resembling an apophysis, and the rough surface of the stems, were present in the newly gained specimens as in the former ones. Finally it must be stated that the sclerotia with which the new experiments were made, originated from pure cultures and that between the microscopical structure of the former and the new cups and stems no difference was found.

**Physiology.** — “*The cause of sleep.*” By Dr. A. GORTER. (Communicated by Prof. C. WINKLER).

The different well-known theories about the origin of sleep have hitherto not furnished us with a satisfactory explanation either for the want of sleeping or for the sleeping state. By *anaemia of the brain* quite other symptoms are often presented than by want of sleep, and the former has been recognised as a phenomenon of repose even without sleep. The interruption of continuity in the conduction from the brain to the remaining part of the nervous system was considered already by *Purkinje* as the primal cause of sleep and has been treated of afterwards by *LOUIS MAUTHNER* in an essay on *Nona*. In the latter the hypothesis was put forward that the interruption of the contact occurred in those places where, in cases of *Polio-encephalitis haemorrhagica*, the focusses of disease were found<sup>1)</sup>. This theory has more recently found a powerful supporter in *DUVAL*,

<sup>1)</sup> Wien, Med. Wochenschrift 1890 no 23—27.

who in 1895 defended the thesis that the interruption of contact is caused by retraction of the end-arborisations of the neura.

This retraction of the end-arborisations however has never yet been observed, and might be, if occurring, a consequence of sleep, but the investigations of APATHY and BETHE (1894), who hold that the fibrils of different neura pass into one another, have rendered it probable that the causation of sleep is not to be found in this domain.

By the *third theory* the origin of sleep is ascribed to the effect of so-called fatigue-substances, which are presumed to be produced by different functions during the waking state.

Injections of lacteal acid, the sole known fatigue-substance, meanwhile offered only a negative result, moreover this theory is not quite in accordance with the facts:

1<sup>st</sup>. Because during sleep principally such functions are disturbed as are dependent on momentaneous stimuli, i. e. the psychical functions, whilst other functions dependent on stimuli (nutrition etc.) received during the waking state, e.g. respiration, heart-movement, secretion of sweat and urine, digestion etc., are influenced in a lesser degree and may be brought likewise to decreased intensity by repose without sleep.

2<sup>nd</sup>. Because the want of sleep and the duration of sleep are neither of them adequate to the performed psychical and physical labour.

3<sup>rd</sup>. Because sleep may be interrupted at any time by a strong stimulus, the functions operating immediately afterwards in a perfectly normal manner.

4<sup>th</sup>. Because among psychical functions those, originating partly in preceding stimuli, still remain possible (dreams).

5<sup>th</sup>. Because in the case of a new-born babe the want of sleep and the duration of sleep both *diminish* with *increasing functions*.

The insufficiency of these different theories about the origin of sleep have led the physiologist LEONARD HILL to the conclusion: the causation of sleep must still be regarded as metaphysical<sup>1)</sup>.

Meanwhile physiological psychology had taught us that the waking state is consequent on the conduction of stimuli from the surroundings to the central nervous system, and as regards man to the psychical centra, a fact in perfect accordance with the experience that the originating of sleep is favoured by darkness, monotonous sounds and silence. The famous experiment of STRÜMPPELL<sup>2)</sup>, who

1) The Lancet 1890. I. p. 285.

2) Deutsches Archiv. für Klin. Medicin, 1878 No. 22.

transported an almost wholly anaesthetical woman into instantaneous sleep by shutting her one eye and her one ear still capable of seeing and hearing, and who caught from another similar patient the expression:

„Wenn ich nicht sehen kann, dann bin ich gar nicht“, furnished another inducement to seek in cessation of stimuli the causation of sleep.

The well-known manner in which patients are transported into hypnotical sleep, and the fact that by eliminating all external stimuli, animals may be brought to a state closely resembling sleep, both point to the same conclusion.

ZIEHEN schreibt: <sup>1)</sup> „Wahrscheinlich ist das Wesentliche bei dem Zustandekommen des Schlafs, der Abschluss äusseren Reize und die Ermüdung der Rindenzellen.“

HERMANN <sup>2)</sup> „Die nähere Ursache welche die Grosshirnrinde ausser Thätigkeit setzt ist unbekannt. Die meisten Angaben über Veränderungen im Gehirn sind unbewiesene und zum Theil höchst unwahrscheinliche Vermutungen. Die oben angegebenen Thatsachen zeigen dass Schlaf und Wachen im engsten Zusammenhang mit den Sinneseindrücken stehen und man könnte sagen dass zur Erhaltung der gewöhnlichen Thätigkeit der Rinde d. h. des wachen Zustandes beständige Sinneseindrücke nöthig sind, womit aber das Räthsel keineswegs gelöst ist.“

STRÜMPPELL concludes his well-known article in the *Deutsches Archiv* <sup>3)</sup> with these words:

„Eine Reihe von Erscheinungen wie das mögliche Einschlafen trotz stärkeren äusseren Reize, die Periodicität u. a. bedürfen zu ihrer Erklärung noch andere Voraussetzungen.“

Sleep by intoxication (narcotics), and sleep in some cases of brain-disease, may be explained by the interrupting of the conduction of stimuli towards and within the psychical centra. The almost uninterrupted sleep of the new-born babe also may find a similar explanation in the still unfinished cortex.

It becomes moreover difficult to continue searching for the causation of sleep in a peculiar state of the cortex, since dogs, whose brain had been taken away, have been found to present a relatively regular alternating of sleep and waking.

Sleep therefore may be said to be caused either by disease, by intoxication, or by cessation or decrease of stimuli from the surroundings.

<sup>1)</sup> TH. ZIEHEN. Leitfaden der Physiologischen Psychologie p. 218.

<sup>2)</sup> HERMANN, Lehrbuch der Physiologie, p. 460.

<sup>3)</sup> D. Archiv f. klin. Medicin, No 22 p. 350.

*Normal* sleep is not caused by disease, neither, to our knowledge at least, by intoxication, consequently it may be caused by cessation or decrease of stimuli from the surroundings, and in examining these surroundings, we observe the periodically operating cause of sleep in all nature, in

*The setting of the sun*

with which numerous stimuli either disappear or cease to operate. The peculiar characteristic of sleep, the disturbed functions, may be satisfactorily explained by the decrease of stimuli occasioned by the setting of the sun.

Many functions of the living organism depend on sunlight, and when sunlight disappears, their intensity diminishes or they may even cease altogether.

The assimilation of plants, the search for nourishment by animals, the receiving of stimuli by which psychical functions are originated, all these are dependent on sunlight.

The phenomena of sleep having been once recognised as symptoms of decreased functions, all researches for the species of animals in which sleep begins, must necessarily remain fruitless, because most functions of both plants and animals in general are subject to a change, corresponding to the alternation of day and night.

These stimuli which still continue, operating during sleep, partially entertain all functions, the psychical ones included, as we are made to know by experience when dreaming.

The want of sleep in man is a quality inherited from the animal, and it does not appear so directly dependent on the setting of the sun as is the case in vegetal and animal kingdom, only because man continues his struggle for life with the aid of artificial light.

In my opinion, the setting of the sun suffices to explain the periodicity of sleep, and going to sleep notwithstanding the excitation of still extant powerful stimuli, must be accounted for by heredity, and I think the solution of the enigma mentioned by HERMANN, is found here.

The simplicity of this answer to the question about the causation of sleep, presenting itself as a matter of course and reminding one of the egg of Columbus, is only an apparent one, because the results of years of psychological researches have taught us to seek for this causation *outside* the functions, physiology having sought vainly for an explanation to be furnished by the functions themselves.

The existence of night-animals may be explained in this way that

in the struggle for life the dangers threatening them in the day-time, have led certain species of animals to shorten the day and adequately to lengthen the night, in the course of which process qualities were slowly developed, enabling them to carry on with more surety that struggle at night, whilst the want of sleep was satisfied during day-time.

As regards the phenomena of winter-sleep and summer-sleep, both may be considered as a state of torpor, being no real sleep, and in all probability originated again in the struggle for life by certain animals digging themselves into the earth, after their having been driven away by stronger species to regions, either too cold or too hot. Only the strongest individuals survived, and after the lapse of a long period, their progeny may have gradually attained to the power of remaining alive, for a definite space of time, almost entirely without functions, as an hereditary quality, no longer dependent on the influences of heat and cold.

As impossible as it would be for modern man to be kept from sleeping for a somewhat longer period by means of artificial light, as impossible it would be to keep a winter- or summersleeper out of its state of torpor by means of heat or cold, once the season for that state having returned.

It is not known to us whether amongst animals living underground or in the deep of the sea, there exist any species capable of living without sleep.

Until a period not so very long ago, sleep for the greater part of humanity was wholly determined by the sun. During summer man slept little, during winter much, and even in our modern times the peasant does not consult science about the term of duration of his sleep, as his period of sleeping is determined by the sun. The stimuli that keep him awake (issuing from his soil, his cattle and his machinery), all cease to operate with the setting of the sun, consequently he goes to sleep and is awakened again by the stimulus of the sunlight, either directly or indirectly by intermediary of animals.

In modern times the way in which by far the greater majority of men are living, gives rise to the question whether the want of sleep in man may not perhaps wholly or partially disappear in the course of the struggle for life, because we know that inherited qualities tend to disappear, when they are no longer of use in that struggle.

Partly at least this want of sleep has already been conquered in many instances: numerous men are night-animals, sleeping only for a short period in the day-time, others continue to enjoy unimpaired

health, whilst sleeping only for three or four hours out of the twenty-four. Whether in coming generations sleep may be destined to vanish altogether, cannot be predicted with any certainty, because we don't know the exact significance of sleep in the struggle for life in its connection with the longer or shorter term of duration of human life, and because on the other hand we are not sure whether some physiological process does not perhaps continue to operate in the human organism, parallel with and dependent on the alternating of day and night.

The fact may be simply stated that man is the only creature living upon the surface of the earth, capable of making himself no longer dependent on the setting of the sun, by means of artificial light, thus forcing the most intense stimuli to act without interruption on his nervous system. From the point of view of modern science therefore the possibility cannot be excluded, that in some remote future a race may exist, descended from man that will have conquered the want of sleep, the term of duration for individual life, however, having become shortened. In this way the knowledge of the primal cause of sleep in nature, opens a distant prospect of the entire disappearance of sleep in man, who nevertheless, because of reasons mentioned already, will never be able to pass the first weeks of his life in a state of waking.

*Leiden, June 1903.*

**Chemistry.** — *“The condition of hydrates of nickel sulphate in methylalcoholic solution.”* By Prof. C. A. LOBRY DE BRUYN and C. L. JUNGUS.

1. It is known that the old question of the relation between a dissolved substance and a solvent has been answered from two points of view. Whilst particularly of late years, some have defended the theory that the solvent is, as it were, merely a diluent which keeps the dissolved molecules apart without entering into a closer relation with them, others have upheld the view that the molecules of the dissolved substance are most decidedly more or less strongly united to those of the solvent. Owing to the development of the ionic theory, the first assumption is now the more universal one particularly for solutions of salts and their hydrates. On the other hand it must be acknowledged that no strong evidence has ever been brought forward to show the existence of hydrates of salts in an aqueous solution even though it seems natural to presume that to a certain extent

hydrates are already present as such in solutions from which they crystallise and which are in equilibrium with them.

2. It might be expected that the study of solutions of hydrates of salts in a solvent other than water would contribute to the elucidation of the problem. In view of this, one of us <sup>1)</sup> had already been engaged some ten years ago with determinations of the elevation of the boiling point caused by the introduction of hydrates of nickel-sulphate into absolute methylalcohol. The preliminary conclusion then arrived at, led to the assumption that a definite quantity of the water (about 3 mols.) remained in combination with the  $\text{NiSO}_4$ .

In calculating the results of the experiments no notice was taken of certain *factors*, the importance of which was unknown or but little appreciated in 1892, namely the occurrence of electrolytic dissociation, even in alcoholic solution and the influence of a dissolved volatile substance on the elevation of the boiling point. For this reason the former experiments were recalculated and partly extended.

3. In view of the last mentioned fact, we started with the determination of the change in the boiling point caused by the introduction of small quantities of water into absolute methylalcohol. The following result was obtained (Barometer constant).

$\text{CH}_3\text{OH}$ .	$\text{H}_2\text{O}$ .	Elevation of Boiling point	Elevation for 1 pCt.	
55.16 Grm.	0.5720 Grm.	0.291	0.281	} Average 0.281
54.89	0.6799	0.353	0.285	
54.62	0.7866	0.416	0.289	
54.35	0.8877	0.457	0.280	
54.08	1.0378	0.528	0.275	
53.81	1.2127	0.627	0.278	
53.54	1.3831	0.725	0.281	
53.27	1.5565	0.819	0.280	

These experiments, therefore, confirm the conclusion that water added to methylalcohol causes an elevation of the boiling point from the commencement and that no minimum boiling-point occurs here as in the case of ethylalcohol and water (containing about 96 percent of alcohol) <sup>2)</sup>.

<sup>1)</sup> LOBRY DE BRUYN, *Handelingen 4e Natuur- en Geneeskundig Congres, Groningen, 1893*, p. 83.

<sup>2)</sup> W. A. NOYES and WARFEL, *J. Amer. Ch. Soc.* **23**, 463 (1901). SYDNEY YOUNG and EMILY FORTEY, *J. Ch. Soc.* **81**, 717 (1902). The addition of 20 milligrs. of water to 50 grms of methylalcohol caused a perceptible elevation of the boiling-point.

4. As regards the extent of the electrolytic dissociation we observe that although we have not succeeded in determining the amount <sup>1)</sup> the experiments have shown that it is very small. Its existence, moreover further strengthens the conclusion to which the experiments have led, namely that a certain proportion of the water remains in combination with the nickelsulphate.

5. The experiments have been made as before, in the first place with the hydrates  $\text{NiSO}_4 \cdot 6 \text{ aq.}$  and  $\text{NiSO}_4 \cdot 7 \text{ aq.}$ ; a single experiment was made with  $\text{NiSO}_4 \cdot 3 \text{ H}_2\text{O} \cdot 3 \text{ CH}_3\text{OH}$ .

The manner in which the calculation was conducted will be seen from the following example:  $x$  represents here the number of mols. of water abstracted from the hydrate <sup>2)</sup>.

59.9 gr.  $\text{CH}_3\text{OH}$ , 0.7723 gr.  $\text{NiSO}_4 \cdot 6 \text{ aq.}$

(mol. elevation of b. p. of meth. alc. 8.8. Mol. weight  $\text{NiSO}_4 \cdot 6 \text{ aq.} = 262$ )

observed elevation of boiling point =  $0^\circ.165$

Calculated elevation of boiling point supposing all the water

$$\text{had remained in combination } \frac{0.7723}{262} \times \frac{100}{59.9} \times 8.8 = 0^\circ.043$$

elevation of b. p. caused by water delivered by the salt =  $0^\circ.122$

With this corresponds a quantity of water in solution of  $\frac{0.122}{0.281} \%$ .

The abstraction per mol. of dissolved hydrate is, therefore,

$$x = \frac{0.122}{0.281} \times 0.599 \times \frac{262}{0.7723} \times \frac{1}{18} = 4.9 \text{ mol. H}_2\text{O.}$$

The results of the following experiments were:

Methylalc.	$\text{NiSO}_4 \cdot 6 \text{ aq.}$	Elevation of b. p.	$x$ .
58.5 gr.	0.608 gr.	0°143	5.4
60.5 »	0.694 »	0.146	4.9
60.5 »	0.551 »	0.125	5.3

Average from four experiments 5.1

$\text{NiSO}_4 \cdot 7 \text{ aq.}$  gave the following results:

Meth. alc.	$\text{NiSO}_4 \cdot 7 \text{ aq.}$	Elevation of b. p.	$x$ .
60.7	0.432	0°102	6.25
60.7	0.463	0.109	6.2
60.3	0.449	0.110	6.45
60.6	0.481	0.105	5.65
61.7	0.341	0.080	6.3
61.7	0.560	0.120	5.7

Average 6.1

<sup>1)</sup> See next communication.

<sup>2)</sup> Strictly speaking, the elevation of the boiling point caused by the same amount of water will be modified in a slight degree by dissolving the salt in methylalcohol. This influence was not taken into account; the slight amount of electrolytic dissociation (see next article) was also disregarded.

From both experiments the conclusion may be drawn that the hydrates of nickelsulphate when dissolved in methylalcohol only retain one mol. of water of crystallisation. An experiment made with  $\text{NiSO}_4 \cdot 3 \text{H}_2\text{O} \cdot 3 \text{CH}_3\text{O}$  gave as result  $x = \pm 2$  and thus confirmed the above conclusion.

6. If now in a one per cent solution of the hydrates of nickelsulphate in methylalcohol the salt still retains one mol. of water notwithstanding the extreme dilution, it may in our opinion be taken for granted that such is also the case in aqueous solutions. And now proceeding to concentrated and saturated solutions of hydrates we arrive at the notion that the salt-molecule enters into a more or less fixed combination with the water molecules and that, therefore, the hydrates (several simultaneously) are already present as such to a certain extent in the solutions from which they crystallise. Probably there exists in such a system a highly complicated condition of equilibrium.

Some years ago PICKERING has proved by determinations of the freezing points of solutions of sulphuric acid (of different concentrations) in glacial acetic acid that a definite amount of water remains in combination with the sulphuric acid.

Amsterdam, June 1903.

Organ. Chem. Lab. University.

**Chemistry.** — “*The conductive power of hydrates of nickelsulphate dissolved in methylalcohol.*” By Prof. C. A. LOBRY DE BRUYN and Mr. C. L. JUNGUS.

The determination of the conductivity of hydrates of nickelsulphate dissolved in methylalcohol is important for two reasons. Firstly, in order to ascertain whether the condition of the dissolved substance is modified after a shorter or longer period; secondly to ascertain if possible (in connection with the preceding paper) to what extent the salt is dissociated electrolytically.

1. As regards the first point we recall the phenomenon that after dissolving the sulphates (of Cu, Zn, Co, Mg, Ni) in absolute methylalcohol the solutions (some rapidly, others slowly) deposit <sup>1)</sup> lower hydrates or mixed alcoholhydrates; for instance from a solution of

<sup>1)</sup> LOBRY DE BRUYN, Recueil, **11**, 112 (1892) and Handelingen, 4e Natuur- en Geneeskundig Congres, Groningen, 1893, p. 83.

$\text{Ni SO}_4, 7 \text{ aq.}$  or  $\text{Ni SO}_4, 6 \text{ aq.}$   $\alpha$  we obtain after some time crystals of  $\text{Ni SO}_4, 3 \text{ H}_2\text{O}$ ,  $0.3 \text{ CH}_4\text{O}$ . It is however not impossible that, after dissolving, the hydrate loses water with a certain rapidity and combines with the methylalcohol so that a definite stationary condition is not attained immediately. If such were the case we might expect that this modification in the condition of the solution would become evident, say, by a change in the conductive power.

In carrying out the experiments the conductive power was first determined as quickly as possible after preparing the solution (after about 7 minutes). A portion of the solution (which contained about 5% of the salt) was set aside at the ordinary temperature or boiled for 15 minutes. In the latter case the solution was made up again to its original weight. In no cases was a change of the conductivity observed. The same applies to the methylalcoholic solutions of the sulphates of copper and magnesium. The latter exhibits the peculiarity of becoming turbid on heating to  $60^\circ$  and of clearing again on cooling; it was again proved that after heating at  $60^\circ$  for 7 minutes and subsequent cooling the conductive power remained unchanged.

From these experiments we may therefore draw the conclusion that a stationary condition has very probably set in immediately after the sulphates have dissolved in the methylalcohol and that the crystallisation of lower hydrates or of alcoholhydrates, which sometimes occurs after a long time, must be looked upon as a phenomenon of retardation.

2. Secondly, the conductive power was determined of  $\text{NiSO}_4, 7 \text{ aq.}$ ,  $\text{NiSO}_4, 6 \text{ aq.}$ ,  $\text{NiSO}_4, 3 \text{ aq.}$ ,  $3 \text{ CH}_4\text{O}$  and  $\text{NiSO}_4, 1 \text{ aq.}$  dissolved in absolute methylalcohol and at decreasing concentrations. As observed, these determinations were made with the object of studying the extent of the electrolytic dissociation of nickelsulphate in methylalcohol (in connection with the contents of the preceding article). Previous researches, particularly those of CARRARA, had led to the result that, at least with salts composed of univalent ions, the electrolytic dissociation is very considerable, in many cases about  $\frac{2}{3}$  to  $\frac{3}{4}$  of that in aqueous solution. In the case of salts with a bivalent ion the conductive power in methylalcohol is considerably smaller<sup>1)</sup>; that of salts composed of two bivalent atoms has, as far as we are aware, not yet been investigated in methylalcohol solution.

The experiments were made at  $18^\circ$  according to the usual method of KOHLRAUSCH—OSTWALD; the methylalcohol (sp. gr. 0.7397 at  $18^\circ$ )

<sup>1)</sup> COFFETTI, Gazz. Chim. 33, 56.

was again fractionated after addition of some sulphuric acid; the  $\mu$ 's have been corrected for the small remaining conductivity of the alcohol.

With  $\text{Ni SO}_4$  6 aq. pure methylalcohol was used as diluting agent in one series; in a second series an alcohol was used containing the same amount of water as that generated by the hydrate on dissolving. The methylalcohol used for the experiment with  $\text{Ni SO}_4$  1 aq. had been purposely rectified over anhydrous coppersulphate.

The following table contains the results of the measurements.

V	$\text{Ni SO}_4$ 6 aq. Anhydrous $\text{CH}_3\text{OH}$		$\text{Ni SO}_4$ 6 aq. $\text{CH}_3\text{OH}$ with 1.36 vol. % $\text{H}_2\text{O}$ .		$\text{Ni SO}_4$ 3 M. 3 aq. Anhydrous $\text{CH}_3\text{OH}$		$\text{Ni SO}_4$ 7 aq. Anhydrous $\text{CH}_3\text{OH}$ .		$\text{Ni SO}_4$ 1 aq. Anhydrous $\text{CH}_3\text{OH}$ .	
	$\mu$	$\Delta \mu$	$\mu$	$\Delta \mu$	$\mu$	$\Delta \mu$	$\mu$	$\Delta \mu$	$\mu$	$\Delta \mu$
8	3.22	—0.66	3.21	—0.58	—	—	3.22	—0.66	—	—
16	2.56	—0.63	2.63	—0.55	2.54	—0.60	2.56	—0.65	—	—
32	1.93	—0.32	2.08	—0.30	1.94	—0.32	1.91	—0.38	2.11	—0.32
64	1.61	—0.13	1.78	—0.06	1.62	—0.13	1.53	—0.15	1.79	—0.09
128	1.48	+0.02	1.72	+0.15	1.49	+0.02	1.38	+0.05	1.70	+0.06
256	1.50	+0.21	1.87	+0.43	1.51	+0.17	1.43	+0.20	1.76	+0.25
512	1.71	+0.41	2.30	+0.75	1.68	+0.20	1.63	+0.64	2.01	+0.55
1024	2.12	+0.52	3.05	+1.13	1.88	+0.24	2.27	+0.42	2.56	+0.80
2048	2.64	+0.97	4.18	+2.44	2.12	—	2.69	—	3.36	—
4096	3.61	—	6.62	—	—	—	—	—	—	—

From the figures given it will be seen that the object of the investigation, that is to say the determination of the extent of the electrolytic dissociation, has not been attained because we meet with the peculiar phenomenon that the conductive power at first decreases and that for  $v=128$  a minimum for  $\mu$  occurs; on further dilution the conductivity again increases but a  $\mu \infty$  cannot be determined. We cannot, at present, account for this occurrence of a minimum which appears in the case of all the hydrates at the same concentration ( $v=128$ ) and is consequently a definite property of nickelsulphate.

We further notice also that the conductivity of nickelsulphate in methylalcohol (also when this contains a few per cent of water)

is very small, many times smaller than that of salts with univalent ions, and at least 20 times smaller than in water. It is for this reason that we have thought proper to disregard the influence of the ionic dissociation on the results given in the preceding communication. Moreover, this influence would only strengthen the conclusion arrived at in that paper.

Amsterdam, June 1903.

*Organ. Chem. Lab. University.*

**Chemistry.** — “*Do the Ions carry the solvent with them in electrolysis?*” By Prof. C. A. LOBRY DE BRUYN.

It is generally known that the behaviour of electrolytes in solution has in many respects not yet been elucidated. We know, for instance, that strongly dissociated electrolytes do not conform to OSTWALD'S law of dilution. In view of this, H. JAHN<sup>1)</sup> some time ago developed a theory in which he attributes this “deviation” to a mutual interaction of the ions, whilst NERNST<sup>2)</sup> also assumes interaction between the ions and the non-dissociated molecules.

A priori it did not appear to be impossible that the ions might exert an action on the molecules of the solvent which would cause them to carry the solvent with them during the electrolysis. If this were found to be the case, it would have to be taken into account in the study of the phenomena of electrolysis.

The question whether the ions carry with them during electrolysis one or more molecules of the solvent cannot as a matter of fact be studied by using purely aqueous solutions, but it can be done by means of solutions of an electrolyte, say, in mixtures of water and methylalcohol. Then if one of the ions carried with it one of the solvents, this would be found out by the difference in the proportion of the two solvents at the cathode and the anode both by comparing them with each other and with the original solution<sup>3)</sup>.

In the research an apparatus of the usual kind was employed such as is used for the determination of the transport numbers of

1) Z. ph. Ch. 36. 458, 37. 490, 38. 125. 2) Ibid. 38. 487.

3) When the experiments were already in progress Prof. ABEGG told me that Prof. NERNST had already made similar experiments using water + mannitol as solvent. These experiments, which only appeared in the Göttinger Nachrichten [1900. 68] had not led to a definite conclusion; Prof. NERNST confirmed this statement. J. TRAUBE (Chem. Zt. 1902, 90) also thinks it probable that each ion is in unstable combination with one molecule of the solvent.

ions (capacity 150 cc.); a few experiments were made with a larger pattern (capacity 450 cc.) As solvent a mixture of methylalcohol and water was used of three different concentrations.

As electrolyte, cuprichloride was first used; when this substance appeared to be unsuitable for the purpose (owing to formation of cuprouschloride) silvernitrate was taken. This salt was sufficiently soluble in the diluted methylalcohol and did not seem to affect it during the electrolysis. The electrodes were made of silver, the cathode was placed in the uppermost limb of the apparatus and the anode, around which the increase of concentration of the silvernitrate takes place, in the other. After placing the apparatus in the waterbath a current of 70 volts was passed for 3 to 4 hours; the strength of the current was determined by means of a milli-ampère-meter.

Separate experiments had shown that the methylalcohol could be very accurately determined by distillation. The liquid to be analysed (25 cc. of the cathode- and anode solutions) was mixed with 25 cc. of water and of this mixture 25 cc. were very carefully redistilled into a weighed measuring flask. The amount of silvernitrate was found by titration and the silver deposited on the cathode was weighed. From the following particulars of the experiments, we may draw the conclusion that under the circumstances of the experiments there is no question of a transference of the solvent along with one of the ions.

It was found previously that on dissolving  $\text{AgNO}_3$  in dilute methylalcohol the volume of the liquid is scarcely affected. Methylalcohol of 25 pCt. by weight.

Weight of measuring flask after distillation from solvent	36.838
" " " " " " " solution n. $\text{AgNO}_3$	} 36.872
	} 36.879

I. Meth. alc. of 25 pCt. by weight. Small apparat. Curr. 0.36 ampères.

Time:  $3\frac{1}{2}$  hours. Silver on the cathode: 4.50 grams.

Conc.  $\text{AgNO}_3$  before the experiment: normal.

Conc. $\text{AgNO}_3$ after	" "	{ anode 1.30 normal
		{ cathode 0.54 "

Weight of measuring flask after the distill.	{ solution at anode 36.876
	{ " " cathode. 36.875

II. Meth. alc. 35pCt. by weight. Large apparatus. Current 0.32 ampère.

Time: 4 hours. Silver at cathode: 4.1 grams.

Conc. of  $\text{AgNO}_3$  before the experiment: normal.

" " " after " " { anode 1.37 normal  
 cathode 0.94 "

Weight of measuring flask after the distill. { original solution 36.498  
 solution at anode 36.508  
 " " cathode 36.503

III. Meth. alc. of 64 % by weight. Small apparatus. Current 0.15 ampère. Time:  $3\frac{1}{2}$  hours. Silver on the cathode: 1.80 gr.

Conc. of silver before the experim.: normal.

" " " after " " { anode:  $\text{AgNO}_3$  crystal. out  
 cathode: 0.73 normal.

Weight of measuring flask after the distill. { original solution 35.100  
 solution at anode 35.100  
 " at cathode 35.094

By an easy calculation we now find that if for instance, the  $\text{Ag-}$  or  $\text{NO}_3\text{-}$ ion had carried with it one molecule of the solvent, for every 4 grams of silver an increase or decrease of 0,6 to 0,7 gr. of water or of about 1.2 grams of methylalcohol at the anode or cathode would have been stated. This would have been plainly detected by the analysis even though the amount had been largely diminished by diffusion <sup>1)</sup>.

I have to thank my assistants Messrs. C. L. JUNGUIS and S. TYMSTRA for their assistance rendered in these experiments.

**Chemistry.** — Prof. C. A. LOBRY DE BRUYN presents communication N<sup>o</sup>. 5 on Intramolecular Migrations: C. L. JUNGUIS. "*The mutual transformation of the two stereo-isomeric methyl-d-glucosides.*"

1. When in 1893 EMIL FISCHER <sup>2)</sup> discovered the glucosides of the alcohols and proposed for these substances a formula deduced by him from the glucose-formula of TOELLENS, namely



he suggested that on account of the appearance of a new asymmetric

<sup>1)</sup> It is possible of course that the two ions act in the same manner and carry with them equal quantities of one of the solvents or of both.

<sup>2)</sup> Ber. 26. 2400.

carbon-atom two stereo-isomeric glucosides ought to be capable of existence. These two isomers would then be comparable to the two penta-acetates then known.

About a year afterwards, ALBERDA VAN EKENSTEIN<sup>1)</sup> succeeded in obtaining this second isomer  $\beta$ -methylglucoside. He found that if the reaction between glucose and methylalcohol (with hydrochloric acid as catalyser) was stopped the moment that all the glucose as such had disappeared, the two isomers were both present, the  $\alpha$ -form being predominant. They could be separated by fractional crystallisation. He further noticed that the  $\beta$ -form passes into the  $\alpha$ -form in presence of a solution of hydrochloric acid in methylalcohol; if, therefore, the reaction is continued for a long time, we observe that the rotation increases [the  $[\alpha]_D$  of the  $\alpha$ -isomer is  $+158^\circ$ , that of the  $\beta$ -isomer  $-32^\circ$ ] whilst the  $\beta$ -methylglucoside disappears more and more.

The  $\beta$ -isomer therefore appeared to be the metastable and the  $\alpha$ -isomer the stable form.

The observations of ALBERDA lead to the conclusion that, as in so many analogous cases, the so-called metastable form is here the first product of the reaction and that the isomer is produced from this afterwards.

It now became important to further investigate the transformation of the one isomer into the other with a view both to its velocity and to the influencing factors. The view propounded by EMIL FISCHER<sup>2)</sup> that glucosdimethylacetal  $\text{CH}_2\text{OH}-(\text{CHOH})_4\text{CH}(\text{OCH}_3)_2$  may be the intermediate product in the formation of the two glucosides might be tested by an investigation of this kind. This acetal is a syrupy liquid which occurs as the first product of the action of methylalcoholic hydrochloric acid on glucose; it does not react with phenylhydrazine or FEHLING'S solution and is very readily reconverted into glucose by the aqueous acids; it was however not obtained pure and not analysed. As this substance, supposed to be the dimethylacetal, was converted into the two glucosides on warming with methylalcoholic hydrochloric acid, the transformation being however not complete and as moreover the two other substances were obtained when starting from one of the two glucosides, FISCHER concluded: „dass der Vorgang welcher vom Acetal zum Glucosid führt, umkehrbar ist, dass ferner die Verwandlung der Glucoside in einander über das Acetal führt und dass mithin die drei Verbindungen als Factoren

1) Recueil 13, 183.

2) Ber. 28, 1146.

eines Gleichgewichtszustandes resultieren":  $\alpha$ -methylglucoside is then always present in the largest quantity.

2. My research has now led to the following results.

If we start on the one hand from pure  $\alpha$ - and on the other hand from pure  $\beta$ -methylglucoside<sup>1)</sup> the methylalcoholic solution of HCl arrives in both cases at the same condition of equilibrium in which the  $\alpha$ - and  $\beta$ -compounds are both present. After removing the HCl with  $\text{PbCO}_3$  and evaporating the solvent a crystalline mass was left which was extracted with acetic ether. This on evaporation yielded an extremely small quantity of a non-crystallisable product [at most 10 milligr. from 2.5 gram of  $\alpha$ -glucoside] which may possibly be FISHER's dimethylacetal. Its concentration is, therefore at any rate exceedingly small in comparison with those of the two glucosides.

3. From the rotation of the solution, after equilibrium is attained, it may be found by calculation that 77 % of the glucoside is present in the  $\alpha$ - and 23 % in the  $\beta$ -form.

From the change in rotation with the time the velocity, with which the transformation takes place, may be calculated. It appears that the formula for a non-complete unimolecular reaction is applicable here;

$$\frac{dx}{dt} = k(a - x) - k'(a' + x)^2$$

[ $a$  and  $a'$  are the concentrations of the two glucosides at the moment the measurement begins,  $x$  is the quantity converted after the time  $t$ ].

By integration this formula gives

$$k + k' = \frac{1}{t} \lg \frac{x_\infty}{x_\infty - x};$$

$x_\infty$  is the total quantity converted from  $t = 0$  to  $t = \infty$ .

$k + k'$  remained satisfactorily constant during the reaction both when the  $\alpha$ - and when the  $\beta$ -glucoside was used, and led in both cases to the same figure. With a 1.34 normal solution of HCl in methylalcohol  $k + k'$  at 25° was found to be 0.0051; (the time expressed in hours); the transformation at that HCl-concentration therefore proceeds tolerably slowly; the equilibrium is practically attained after about 20 days.

4. The result of the velocity determinations is most simply expressed by supposing that the reciprocal transformation of the two isomers represents an intramolecular migration, in this way:  $\alpha \rightleftharpoons \beta$ . The in-

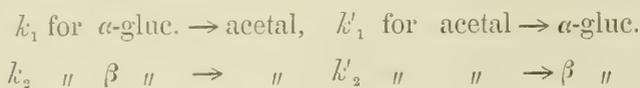
1) I have to thank Mr. ALBERDA VAN EKENSTEIN for kindly supplying me with a certain quantity of these two substances.

2) This formula has been first applied by KISTIAKOWSKY to esterification.

intermediate occurrence of acetal is improbable; we should then have the reaction:  $\alpha \rightleftharpoons \text{acetal} \rightleftharpoons \beta$ . The quantities measured being the velocities with which  $\alpha$  or  $\beta$  disappears and  $\beta$  or  $\alpha$  appears. It would satisfy the formula for the reversible unimolecular transformations only if the acetal was converted with an immeasurably great velocity into  $\beta$  or  $\alpha$ . An attempt was made to elucidate this question by means of a separate experiment. Supposing the mechanism of the transformation to be really:



we should then have two equilibrium reactions for which there would exist four velocity constants.



As it had, however, been ascertained that in the condition of equilibrium, acetal is practically absent, the limit for the two equilibrium reactions is situated close to the two glucosides; from this follows that the ratios  $\frac{k'_1}{k_1}$  and  $\frac{k'_2}{k_2}$  must be very large. This is only possible if  $k_1$  and  $k_2$  are very small or in other words if the transformation, setting out from either of the glucosides, proceeds very slowly, or if  $k'_1$  and  $k'_2$  are very large, that is to say if the acetal is converted with extraordinary rapidity into the two glucosides. From the results of the velocity determinations already given, it follows that the first possibility does not exist; to test the second supposition, the non-crystallisable substance, which FISCHER reservedly considered to be the possible dimethylacetal of glucose was prepared according to his directions. The syrup obtained by extraction with acetic ether was laevorotatory [it however still reduced FEHLING'S solution slightly]; it was dissolved in 2 *n.* methyl alcoholic hydrochloric acid (about 2,5 gr. in 25 c.c.m.) and the change at the ordinary temperature was observed. This took place by no means rapidly.

Rotation :	$t = 0$	$-1^{\circ}.0$	$t = 19$	hours	$+17^{\circ}.5$
	$= 12$	$+0^{\circ}.7$	26.5	"	$19^{\circ}.9$
	$= 2$	$+5^{\circ}.5$	43	"	$22^{\circ}.9$
			67	"	$26^{\circ}.0$

Everything considered it must be assumed to be very improbable that the syrupy substance [perhaps the acetal] occurs as an intermediate product in the reaction  $\beta \rightleftharpoons \alpha\text{-glucoside}$ . The traces of a syrup which

were found are then due to a secondary reaction which does not interfere with the study of the main reaction.

The conclusion should therefore rather be that the two glucosides are directly converted into each other.

5. The point in question would be solved with complete certainty if the reciprocal transformation of  $\alpha$  into  $\beta$  were observed in another solvent than methylalcohol. Except in water these glucosides are also slightly soluble in ethylalcohol. As aqueous hydrochloric acid causes a resolution into sugar and methylalcohol the behaviour of ethylalcoholic hydrochloric acid was investigated. In this solvent the transformation also proceeded according to the formula for reversible reactions, the same limit being reached as when methylalcohol was used as solvent<sup>1)</sup>.

6. The concentration of hydrochloric acid necessary to cause the mutual transformation of the two isomers to take place with measurable velocity, is tolerably large; much larger than is usually the case in catalytic reactions. The possibility is therefore not excluded that HCl takes part in some unknown way in the reaction. This theory is supported by the strongly retarding influence of water on the mutual transformation.

For a HCl-concentration of 1.07 norm.  $k + k'$  is about 0.0040. In the presence of 1 mol. of H<sub>2</sub>O to 1 mol. of HCl. [about 2 vol. % water] in the solution  $k + k'$  was found to be reduced to 0.0012. If to 1 HCl, 5 H<sub>2</sub>O was added [about 10 vol. % of water], the transformation took place exceedingly slowly,  $k + k' = 0.0001$ ; in this case a little glucose was also formed.

Finally, the constants which have been calculated by means of the formula  $\frac{1}{t} l \frac{x_{\infty}}{x_{\infty} - x}$  for different HCl-concentrations, point to a more rapid increase of  $k + k'$  with the HCl-concentration than that required by simple proportionality:

Concentration HCl	$k + k'$	$\frac{k + k'}{n. \text{ HCl}}$
n. 1.34 (in CH <sub>3</sub> OH)	0.0051	0.0038
» 2.06 ( » )	0.0091	0.0044
» 2.28 (in C <sub>2</sub> H <sub>5</sub> OH)	0.0130	0.0057
» 4.71 ( » )	0.0384	0.0082

<sup>1)</sup> The product obtained was syrupy and crystallised very slowly. Apparently, a little ethylacetal or ethylglucoside must have been formed.

7. With a view of ascertaining whether a transformation was also possible without HCl, the  $\beta$ -glucoside was kept for a long time in a fused condition. After cooling the  $\alpha_D$  appeared to be quite unchanged.

Zinechloride in methylalcoholic solution is also incapable of causing the transformation.

8. In conclusion it may be mentioned that the rotatory power of a solution of methylmannoside [of which glucoside only one form is known as yet] in a solution of hydrochloric acid in methylalcohol gradually decreases without formation of mannose.

It seems natural to assume that this is caused by a partial change into a  $\beta$ -isomer which may, perhaps, also be isolated.

These investigations are being continued.

*Org. Chem. Lab. University.*

*Amsterdam, June 1903.*

**Chemistry.** "*The electrolytic conductivity of solutions of Sodium in mixtures of ethyl- or methylalcohol and water.*" By Mr. S. TIJMSTRA *Bz.* (Communicated by Prof. C. A. LOBRY DE BRUYN).

In his study of the velocity of substitution of one nitro-group in *o*- and *p*-dinitrobenzene by an oxyalkyl<sup>1)</sup> STEGER arrives at the result that the reaction constants of *o*-dinitrobenzene and the two alcoholates Na OC<sub>2</sub>H<sub>5</sub> and Na OCH<sub>3</sub> are not changed by dilution or by addition of a sodium salt. On the other hand, in the formation of ethers, these constants are increased by dilution, as shown by HECHT, CONRAD and BRÜCKNER, and decreased by addition of a sodium salt as demonstrated by STEGER.

LOBRY DE BRUYN pointed out that it would be necessary to investigate the conductivity of Na OC<sub>2</sub>H<sub>5</sub> in alcoholic solution.

In a further investigation of the influence of water on the substitution of the NO<sub>2</sub>-group in *o*-dinitrobenzene by an oxyalkyl<sup>2)</sup> and on the formation of ethers<sup>3)</sup> it appeared; 1<sup>st</sup>. that the velocity coefficients of these reactions remained constant when water was added up to an amount of 50 per cent by weight; 2<sup>nd</sup>. that the addition of water decreased the velocity of reaction of Na OC<sub>2</sub>H<sub>5</sub> but increased that of Na OCH<sub>3</sub> (at least at the commencement, afterwards the velocity

1) Dissertation, Amsterdam, 1898. Recueil **18**, 13. (1899).

2) LOBRY DE BRUYN and ALPH. STEGER, Recueil **18**, 41.

3) LOBRY DE BRUYN and ALPH. STEGER, Recueil **18**, 311.

diminishes again); 3<sup>rd</sup>. that in mixtures of water and alcohol in which Na is dissolved, the sodium alcoholates are still present.

This last conclusion seems at first sight strange. But previous observations had been made which justified the belief that  $\text{Na OC}_2\text{H}_5$  is present in an aqueous-alcoholic solution of sodium. HENRIQUES <sup>1)</sup> for instance showed that in the saponification of fats with aqueous-alcoholic soda the fats are not directly decomposed by the NaOH (the alcohol would then only play the part of a solvent) but that at first the ethyl esters of the fatty acids are formed. The well-known reaction of BAUMANN—SCHOTTEN leads to a similar conclusion.

Some three years after the above mentioned memoirs appeared, LULOF <sup>2)</sup> studied the action of sodium alcoholate on chloro- (bromo- or iodo-) dinitrobenzene (1, 2, 4), and observed the influence of dilution with both absolute and dilute alcohol. It was then shown that the reaction constants are really affected by the concentration which was not the case in STEGER's experiments; decrease of the concentration increases the constant, addition of a salt with a common ion, such as NaBr, decreases the constant both in absolute and dilute ethylalcohol. Here again the water seemed to exert an influence, for in the case of ethyl alcohol a fall in the reaction constants took place whilst with methyl alcohol first a rise and then a fall was noticed. Why all this occurred could not be explained.

From the above facts it was evident (and it was repeatedly pointed out in the papers in question) that it was necessary to study the conductivity of sodiummethylate and -methylate in mixtures of water and alcohol. For this reason I decided to undertake this investigation.

A short review of the results is given in the following tables and the graphical representations connected therewith. A fuller description of the experiments will be given elsewhere.

As starting point I always used solutions which were about  $\frac{1}{1}$  normal, determined their resistance and from the diluted solutions prepared therefrom, I calculated the  $\mu$ 's for those dilutions and determined by interpolation the  $\mu$ 's for the dilutions of 1 molecule in 1, 2, 4, 8, . . . 512 Litres. The experiments were all done at a temperature of 18°.

In the following tables, the figures are represented graphically in Fig. I, II, III and IV, where the  $\mu$ 's are taken as ordinates and the logarithms of the dilutions as abscissae. By using the logarithms the scale of the drawing is reduced. The alcoholic percentages are

1) Z. f. angew. Ch., 1898, 338, 697.

2) Dissertatie, Amsterdam, 1901. Recueil 20, 292. (1901).

by weight and have been determined by means of the specific gravity bottle.

[It is to be noticed that Fig. III is not reproduced on the same scale as Fig. I; since the methyl alcohol curves would intersect and the figure would therefore become confused, the scale of the abscissae has been taken four times larger].

#### Sodium in Ethyl Alcohol + Water.

Percentage of alcohol by weight.	99.44 pCt.	96.54 pCt.	88.85 pCt.	86.50 pCt.	78.83 pCt.	70.40 pCt.	48.18 pCt.	25.14 pCt.
$\mu_{v=1}$	—	5.32	6.866	7.737	11.59	16.40	35.15	70.05
$\mu_{v=2}$	7.602	8.916	11.13	12.44	17.20	23.59	43.59	80.98
$\mu_{v=4}$	10.30	11.99	15.17	16.87	22.44	29.70	49.72	89.08
$\mu_{v=8}$	12.95	14.99	18.72	20.77	26.38	34.54	54.16	94.62
$\mu_{v=16}$	15.79	17.95	22.04	24.29	30.10	38.67	58.07	99.80
$\mu_{v=32}$	18.92	21.21	25.27	27.66	33.48	42.19	61.34	103.4
$\mu_{v=64}$	22.18	24.53	28.59	30.86	36.60	45.22	63.68	107.2
$\mu_{v=128}$	25.41	27.78	31.53	33.73	39.23	47.68	64.89	109.2
$\mu_{v=256}$	28.51	30.82	34.31	36.51	41.52	49.67	65.40	111.2
$\mu_{v=512}$	31.30	33.62	37.04	38.97	43.00	50.81	64.54	112.0

#### Sodium in Methylalcohol + Water.

Percentage of alcohol.	100 pCt.	93.09 pCt.	87.72 pCt.	81.40 pCt.	74.70 pCt.	69.99 pCt.	59.97 pCt.
$\mu_{v=1}$	21.49	22.77	23.89	25.72	27.85	30.21	33.48
$\mu_{v=2}$	31.18	32.66	33.59	35.02	36.92	38.80	42.75
$\mu_{v=4}$	40.38	40.97	41.21	41.97	43.43	45.26	49.01
$\mu_{v=8}$	48.13	47.90	47.03	47.24	48.36	49.93	53.60
$\mu_{v=16}$	54.78	53.63	52.07	51.41	52.37	54.04	57.33
$\mu_{v=32}$	60.77	58.65	56.15	55.03	55.73	57.30	60.47
$\mu_{v=64}$	65.97	63.08	59.64	58.13	58.68	59.79	62.87
$\mu_{v=128}$	70.42	66.98	62.62	60.28	61.00	62.07	64.99
$\mu_{v=256}$	74.50	70.09	64.73	62.12	62.60	63.57	66.40
$\mu_{v=512}$	77.92	72.44	66.49	62.99	63.72	64.55	67.01

From these figures we obtain the important result that methylalcohol differs from ethylalcohol in its behaviour. This is seen at once from the graphical representation in Fig. IV (showing the changes of the  $\mu$ 's, namely of the  $\mu_{v=1}$ ,  $\mu_{v=2}$  etc. with the amount of water). At the gas concentration ( $v = 22$ ) a minimum occurs

with methylalcohol. This minimum is not present in the higher concentrations but at the larger dilutions it becomes more and more evident. This minimum is found precisely in the neighbourhood of those dilutions ( $v = 22$  and higher) at which LOBRY DE BRUYN and STEGER and LULOFS have worked in the experiments referred to above and the amount of water in the alcohol is also the same as that for which these investigators have found the maximum of reaction velocity, namely in 60 to 80 per cent alcohol. There is therefore parallelism between the two phenomena; for methyl alcohol + water + sodium a maximum of the reaction velocity corresponds with a minimum of conductivity.

The experiments are being continued up to pure  $H_2O$  and also extended to mixtures of ethyl- and methylalcohol.

Amsterdam, June 1903.

Org. Chem. Lab. University.

**Physiology.** — *The string galvanometer and the human electrocardiogram.* By Professor W. EINTHOVEN. (Physiological laboratory at Leyden.)

In the Bosscha-celebration volume of the "Archives Néerlandaises" <sup>1)</sup> the principle of a new galvanometer was mentioned and the theory of the instrument dealt with. The practical usefulness of the instrument especially for electrophysiological measurements may be judged from what follows.

It may be remembered that the instrument consists principally of a silvered quartz thread which is stretched like a string in a strong magnetic field. When an electric current is passed through the thread, this latter deflects perpendicularly to the direction of the magnetic lines of force and the amount of the deflection can directly be measured by means of a microscope with an eye-piece micrometer.

What is the sensitiveness that can be obtained in this manner?

Since the above-mentioned publication a number of material improvements have been made in the instrument by which it is possible, for instance, to give a very feeble tension to the string, now a quartz thread  $2.4 \mu$  thick, with a resistance of 10 000 Ohms. If the tension is so regulated that a deflection takes place in from 10 to 15 seconds depending on its amount, every millimetre of the displacement of the image of the string corresponds to a current of  $10^{-11}$  Amp. when a 660-fold magnification is used. As under these circumstances a

<sup>1)</sup> W. EINTHOVEN. Un nouveau galvanomètre. Archives Néerlandaises des sciences exactes et naturelles. Sér. II. Tome VI. p. 625. 1901.

displacement of 0,1 mm. is still noticeable, as will appear from the discussion of the plates, currents of  $10^{-12}$  Amp. can consequently be detected.

As far as is known to the writer, no other galvanometer is capable of demonstrating with certainty such feeble currents. In practical work the string galvanometer must consequently be placed on a line with the most sensitive galvanometers of other construction and must be distinguished from so-called oscillographs which only react on much stronger currents.

The force which deflects the string in a field of 20 000 C. G. S. with a current of  $10^{-12}$  Amp. is very small and works out for a length of 12.5 cm. at  $2.5 \times 10^{-11}$  grammes i. e. four times less than one ten millionth part of a milligramme.

By giving the string a greater tension its movements become quicker but its deflections for equal currents less. It is easy to give the string exactly such a tension that a current of given intensity causes a predetermined deflection, as may appear from the photograms of the two accompanying plates. These photograms were obtained in the same way as the formerly described capillary-electrometric curves<sup>1)</sup>.

The 660-fold enlarged image of the middle part of the string is projected on a slit, perpendicular to the image. Before the slit a cylindrical lens is placed, the axis of which is parallel to it; behind it a sensitive plate is moved in the direction of the image of the string. While the movements of the string are thus registered, at the same time a system of coordinates is projected on the sensitive plate by the excellent method of GARTEN<sup>2)</sup>. Of these coordinates the horizontal lines are obtained by mounting a glass millimetre-scale close before the sensitive plate so that the sharp shadows of the scale-divisions fall on the plate, while the vertical lines owe their origin to a uniformly rotating spoked disc which intermittently intercepts the light falling on the slit. The distance of the vertical as well as of the horizontal lines has in our photograms been taken about one millimetre, every fifth line being somewhat thicker. This latter peculiarity can easily be introduced into the coordinate system by drawing every fifth line in the glass millimetre-scale before the sensitive plate slightly thicker and by also making every fifth spoke of the rotating disc somewhat broader.

1) See various essays in "PFLÜGER'S Arch. f. d. gesamte Physiol." and in "Onderzoekingen physiol. laborat. Leyden." 2nd series.

2) DR. SIEGFRIED GARTEN. Ueber rhythmische elektrische Vorgänge im quergestreiften Skelettmuskel. Abhandl. der Königl. Sächs. Gesellsch. der Wissensch. zu Leipzig. Mathem. phys. Classe, Bd. 26, No. 5. S. 331. 1901.

The first photogram, fig. 1 plate I represents the deflections of the string when currents of 1, 2 and  $3 \times 10^{-9}$  Amp. are successively passed through the galvanometer. In the coordinate system a length of 1 mm. of the abscissae has a value of 0.1 second, an ordinate of 1 mm. representing  $10^{-10}$  Amp. Although the image of the string has considerable breadth and has no perfectly sharp outlines — as must be expected with a magnification of 660 times — yet its displacement in the coordinate system can easily be determined with an accuracy of 0.1 mm. For if one of the margins of the image before and after the deflection is observed, observation with the unaided eye or with a magnifying-glass will show that the deflection differs from the tabulated amount by less than 0.1 mm. Hence the currents are measured in the photogram with an accuracy of  $10^{-11}$  Amp.

One notices that the deflections are accurately proportional to the intensity of the current, that they are dead-beat and that they are accomplished in 1 to 2 seconds according to their magnitude. The strong damping must be ascribed to the resistance of the air, for during the registering of the curves a resistance of one Megohm was put into the galvanometer circuit by which the ordinary electromagnetic damping was almost entirely suppressed.

If the tension of the string is made ten times less, the galvanometer becomes ten times more sensitive and, as stated above, currents of  $10^{-12}$  Amp. may still be observed. But with this greater sensitiveness the deflections are no longer proportional to the current and the movements of the string are difficult to record, as the quartz thread no longer moves exactly in a plane. Yet the instrument can still be used then for direct observation with the microscope.

Figure 2 plate I shows that the deflections to the right and to the left — in the figure corresponding to upward and downward deflections, are equal. The velocity of the sensitive plate has remained the same so that again an abscissa of one millimetre corresponds to a time of 0.1 second. But the tension of the string is 200 times stronger so that one millimetre of the ordinates represents  $2 \times 10^{-8}$  Amp. A current of  $4 \times 10^{-7}$  Amp. is alternately sent in opposite directions through the galvanometer and hence causes deviations of 20 mm. to the right and also to the left. It is easy to ascertain that these deviations are equal to each other up to 0.1 millimetre.

The movement of the string is very quick so that during the deflection the string can only cast a feeble shadow on the sensitive plate. The ascending and descending nearly vertical lines which in the original negative are still visible as very thin streaks have become invisible in the reproduced photogram.

In fig. 3. plate I a movement of the string is represented when a current of  $3 \times 10^{-8}$  Amp. is suddenly made and broken. The sensitive plate has been moved along with a tenfold velocity and the string has ten times more tension than in fig. 1, consequently one mm. absc. = 0.01 second and one mm. ord. =  $10^{-9}$  Amp. The galvanometer circuit contains again one Megohm so that the same causes of damping exist as in fig. 1. The movement is still dead-beat, but on account of the 10 times greater force on the string it is 10 times quicker, as can easily be ascertained by comparing the great descending curve of fig. 1 with one of the curves of fig. 3 or better still by superposing diapositives of the curves of both figures. They will then be seen to cover each other exactly and since in one figure the velocity of the moving plate is ten times greater than in the other, the deflection of the string must in one case take place ten times more quickly than in the other. At the same time the resistance of the air is proved in our case to increase proportionally to the velocity of the string itself.

In recording the curves of fig. 4 and 5 of plate I the velocity of the moving plate has been increased to 250 mm. per sec. so that 1 mm. of the abscissae is 0.004 sec. The plate at first moves slowly and reaches the mentioned velocity only when it has travelled through a distance of 4 or 5 centimetres, whereas the spokes of the rotating disc always cast their shadows on the plate accurately every 0.004 second. Hence the coordinate system is in the first sixth part of the photograph compressed in the direction of the abscissae.

In fig. 4 one mm. ord. =  $2 \times 10^{-8}$  Amp., while in fig. 5 one mm. ord. =  $3 \times 10^{-8}$  Amp. These two figures together show us the limit-value of the sensitiveness for which the movement of the string is still dead-beat. In fig. 4 a current of  $4 \times 10^{-7}$  Amp., in fig. 5 a current of  $6 \times 10^{-7}$  Amp. has been transmitted through the galvanometer and interrupted. One sees that the deflection in fig. 4 is still dead-beat and is completed in about 0.009 sec., whereas in fig. 5 the motion begins to become oscillatory and for a single oscillation takes 0.006 sec. The sensitiveness with which the motion of the string is on the border between aperiodic and oscillatory motion is consequently such that a deflection of one millimetre corresponds to a current between 2 and  $3 \times 10^{-8}$  Amp.

In the tracing of fig. 4 and 5 only an insignificant resistance is put into the galvanometer circuit so that here besides the viscosity of the air also the ordinary electromagnetic damping checks the motion.

Now some particulars may be mentioned referring to the 5 photographs of plate 1 in common.

In order to obtain the image of the string equally sharp in all parts of the visual field, the string must move in a plane perpendicular to the optical axis of the projecting microscope. A displacement of the string of  $0.5 \mu$  in the direction of the optical axis suffices to cause a noticeable indistinctness of the image with the magnification used. The photograms show that such a displacement does not take place.

The great constancy of the zero point and the equality of the deflections deserve notice and also — which is especially important for practical work with the instrument in electro-physiological measurements — the possibility of accurately fixing beforehand the sensitiveness of the instrument. The unaided eye can already observe in nearly all the figures of plate I that this can be done successfully with an error of less than 0.1 mm. for deflections of 30 or 40 mm., i.e. with an error of less than 2.5 or 3 per thousand. Only fig. 5 shows a real deficiency of about 0.1 mm. which some greater care might have avoided.

It is hardly necessary to point out that the galvanometer is not affected by variations in the surrounding magnetic field. Moreover it is not to any extent affected by tremors of the floor. It stands on the same stone pillar on which a large tin disc with spokes is rapidly rotated by an electromotor. This electromotor is only at a few centimetres' distance from the galvanometer, while another motor, coupled with a heavy fly-wheel, for moving the sensitive plate, is clamped to the same pillar at a somewhat greater distance. Yet no trace of mechanical vibrations appears in the photograms.

The first electro-physiological investigation made with the string galvanometer was one concerning the shape of the human electrocardiogram discovered by AUG. D. WALLER<sup>1)</sup>. Until now this could only be obtained by means of the capillary electrometer. But the curve traced by that instrument gives, when superficially observed, a quite erroneous idea of the changes of potential differences actually occurring during the registering. In order to know these they have to be calculated from the shape of the recorded curve and the properties of the capillary used. This leads to the construction of a new curve, the form of which is the correct expression of the actual variations of potential.

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<sup>1)</sup> AUGUSTUS D. WALLER. On the electromotive changes, connected with the beat of the mammalian heart and of the human heart in particular. *Philosoph. Transactions of the Royal Society of London*, vol. 180 (1899), B, pp. 169—194.

An example may explain this <sup>1)</sup>.

The following fig. 1 represents the curve traced for the electrocardiogram of Mr. v. D. W. when the current was derived from

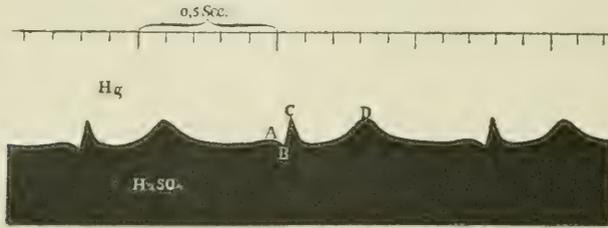


Fig. 1.

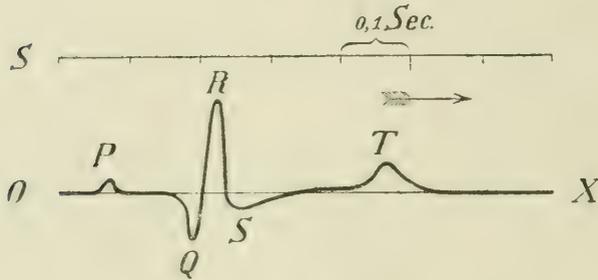


Fig. 2.

the right and left hands, whereas fig. 2 is the constructed curve. The differences are obvious. Especially the tops *C* and *D* in the registered curve should be compared with the corresponding tops *R* and *T* in the secondary curve which latter alone truly represents the ratio of the heights of the tops.

We shall now try to compare the string galvanometer as a research instrument with the capillary electrometer and must first of all bear in mind that the deflections of the string galvanometer measure a current, that of the capillary electrometer an electromotive force. But it must be remarked that whenever variations in current or tension are measured, the mercury meniscus as well as the string moves. And during this movement the capillary must be charged or discharged by an *electric current*, whereas the string in the magnetic field develops an opposed *electromotive force*. Moreover, when there is a constant considerable resistance with negligible self-induction, such as commonly occurs in electro-physiological investigations, the

<sup>1)</sup> See PFLÜGER'S Arch. Bd. 60. 1895 and "Onderzoekingen". Physiol. Laborat. Leyden. 2nd series, vol. 2.

intensity of the current will at any moment be proportional to the active electromotive force, so that the fundamental difference between the electrometer and the galvanometer is no obstacle to a comparison of both instruments.

The string galvanometer has several advantages over the capillary electrometer. First the deflection of the string galvanometer will in many cases and especially in the case of tracing a human cardiogram be greater and quicker than the deflection of the capillary electrometer. Then the capillary electrometer is less accurate in the constancy of its indications, their proportionality to the potential differences and their equality in opposed directions.

A highly magnified image of the mercury meniscus cannot be so sharply projected as that of a fine thread and one cannot regulate the sensitiveness of the capillary electrometer to a predetermined amount. The electrical insulation of the string galvanometer is much easier than of the capillary electrometer and a phenomenon like "creeping" does not occur with the galvanometer.

In the capillary electrometer the movement of the meniscus is damped by the friction of the mercury and sulphuric acid when streaming through a narrow tube. Invisibly small traces of impurities may hinder or even entirely stop the movement of the mercury meniscus. Many a capillary had after a relatively short time to be replaced by a new one because there was a "hitch" in the movement of the meniscus. In the string galvanometer, on the other hand, we have air-damping as well as electromagnetic damping, both of which work with perfect regularity. The electromagnetic damping can moreover be varied at will by changing the intensity of the field and the resistance in the galvanometer circuit.

Plate II contains the electrocardiograms of some six persons, traced by means of the string galvanometer. In the coordinate system an absciss of one millimetre has a value of 0.04 sec., while an ordinate of one mm. represents a P.D. of  $10^{-4}$  Volts. By choosing these round numbers the curves satisfy generally the requirements of the international committee for the unification of physiological methods.

The movement of the quartz thread, as may be seen from the normal curves at the end of each photogram, was dead-beat and very quick, so that the traced electrocardiogram is a fair representation of the oscillations in the potential difference existing between the right and left hands of the experimental person. As a rule this may be admitted for the lower tops *P*, *Q*, *S* and *T* without any noticeable error. But for the high and sharp top *R* a correction should be applied especially in photograms 8 and 9, a correction by which

the extremity of the top would be shifted a little to the left and upwards. The necessary correction is small however and its amount may be approximately estimated at less than 0.2 mm. for the shifting to the left and less than one mm. for the shifting upwards.

Photogram 8 represents the electrocardiogram of the same person whose capillary-electrometric curve is shown in the text. When the registered curve of fig. 8 plate II is compared with the formerly plotted curve of fig. 2 in the text, it is evident that both curves have great similarity. The tops *P*, *Q*, *R*, *S*, and *T* are not only present in both curves, but have also the same relative height in both.

In the plotted curve 1 millivolt of ordinate has been made equal to 0.1 sec. of absciss, while in the galvanometer curve 1 millivolt of ordinate corresponds to 0.4 sec. of absciss. Hence the galvanometer curve is compressed in the direction of the abscissae, as a superficial inspection will reveal. Besides the galvanometer curve, on account of the gradual transitions of one top to another, gives the impression of being in its minor details a more faithful representation of nature than the plotted curve. It is obvious that of this latter curve only a limited number of points could be accurately calculated, while for the rest the calculated points had to be joined by the curve that fitted them best. But these small differences are immaterial.

It may give some satisfaction that the results formerly obtained by means of the capillary electrometer and more or less laborious calculation and plotting have been fully confirmed in a different and simple manner by means of the new instrument. For this affords us a twofold proof, first of the validity of the theory and of the practical usefulness of the formerly followed methods and secondly of the accuracy of the new instrument itself.

The six electrocardiograms of plate II were selected among a greater number and arranged after the dimensions of the downward top *S* (see the figure in the text). In 6 and 7 the curve remains, at the spot where *S* ought to be, above the zero-line of the diastole, in 8 and 9 *S* is only small, in 10 and 11 great. The numbers 6 and 11 mark in this respect the extremes which occur in our collection of electrocardiograms, whereas N<sup>o</sup>. 8, that of Mr. v. D. W. represents a sort of norm with which the other numbers may all be easily compared.

The constancy of shape of the curve for a certain person is remarkable. This shape seems even to change so little in course of time, that with some practice one may recognize many an individual by his electrocardiogram. We conclude this essay with a remark on the

small irregular vibrations occurring in most electrocardiograms, where they sometimes reach a height of 0,1 to 0,5 mm. and more, but are sometimes entirely absent, as e.g. in N<sup>o</sup>. 6 of Mr. AD.

These vibrations are not caused by tremors of the floor or other irregularities which should be ascribed to an insufficient technique as is easily shown by the vibrationless normal curves at the end of almost every series of electrocardiograms. Hence they must be caused by electromotive agents in the human body itself and the question arises whether they find their origin in the action of the heart or of other organs. We may expect that an investigation undertaken with this object will give a definite answer to this question.

**Physics.** — Dr. J. E. VERSCHAFFELT. “Contributions to the knowledge of VAN DER WAALS’  $\psi$ -surface. VII. The equation of state and the  $\psi$ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components.” (part 4). Supplement N<sup>o</sup>. 6 (continued) to the Communications from the Physical Laboratory at Leyden by Prof. KAMERLINGH ONNES.

(Communicated in the meeting of May 30, 1903).

### 17. The $\alpha$ , $\beta$ -diagram.

In the previous communications the different phenomena in the neighbourhood of the critical point in substances with small proportions of one component have, according to our plan set forth at the beginning, entirely been expressed by means of the  $\alpha$  and  $\beta$  and the co-efficients that can be derived from the general empirical reduced equation of state. For shortness, and to avoid the constant repetition of the same factors (comp. §1) I have used till now, instead of the differential quotients of the general empirical reduced equation of state, the co-efficients  $k$ , where the  $m$ 's (comp. form. 19) have been expressed by means of  $\alpha$  and  $\beta$ , but henceforth, as the numerical values are more important I shall make use again of the differential quotients of the reduced equation of state itself, used in equation (1). It seemed important to me to completely determine by means of the numerical values of  $\alpha$  and  $\beta$  the different cases which, according to the formulae found by KEESOM (Comm. N<sup>o</sup>. 75) and by me (loc. cit.), may present themselves in the relative situation of the different critical points. To illustrate this I intend to divide an  $\alpha$ ,  $\beta$ -diagram into fields in which there is a definite relative situation, by means

of lines, as KORTEWEG has done in another diagram (the  $\alpha, \gamma$ -diagram)<sup>1)</sup>.

This investigation showed that the last of the eight cases distinguished by KORTEWEG of which the inconsistency was demonstrated by him for one special case only, did not exist in general, at least for all the equations of state which satisfy the law of corresponding states. Not to make the investigation too elaborate I have compared the situation of the plaitpoint only with that of the critical state of the pure substance, that is to say I have considered the fields within which  $T_{xpl} >$  or  $< T_k$ ,  $p_{xpl} >$  or  $< p_k$  and  $v_{xpl} >$  or  $< v_k$ . I have also determined in which area the retrograde condensation is of the first or the second kind; and lastly I have indicated in the diagram what had been observed experimentally.

*The plaitpoint temperature.* According to form. (59) the plaitpoint temperature of the mixture is higher or lower than the critical temperature of the pure substance as the expression

$$\frac{m_{01}^2 + RT_k m_{11}}{RT_k m_{11}} \alpha = - \frac{m_{01}^2 + RT_k m_{11}}{RT_k k_{11}}$$

is positive or negative; and,  $k_{11}$  being negative,  $T_{xpl} - T_k$  has the same sign as the numerator.

If for shortness we put

$$p_{01} = \frac{\partial p}{\partial t}, p_{11} = \frac{\partial^2 p}{\partial v \partial t}, p_{21} = \frac{\partial^3 p}{\partial v^2 \partial t}, \dots, p_{30} = \frac{\partial^3 p}{\partial v^3}, p_{40} = \frac{\partial^4 p}{\partial v^4}, \text{ etc.}$$

and for convenience we leave out an index which refers to the critical state, because only those values are used which refer to the critical state,

$$m_{01}^2 + RT_k m_{11} = p_{21}^2 [(\beta - p_{01} \alpha)^2 - C_4 p_{11} \alpha], \quad ^2)$$

so that the area, where  $T_{xpl} > T_k$  is separated from that where  $T_{xpl} < T_k$  by a line of which the equation is:

$$(\beta - p_{01} \alpha)^2 - C_4 p_{11} \alpha = 0.$$

This line, a parabola, represented on the annexed plate<sup>3)</sup> by

1) Proc. Royal Acad., Jan. 31, 1903. The  $\alpha$  and  $\gamma$  are connected in a simple linear way with  $z$  and  $\beta$  (comp. the previous communication p. 666).

2) For we have (comp. form. (19):

$$m_{01} = p_k (\beta - p_{01} \alpha), m_{11} = - \frac{p_k}{v_k} p_{11} \alpha, m_{21} = - \frac{1}{2} \frac{p_k}{v_k^2} [p_{21} \alpha + p_{30} (\alpha - \beta)], \dots$$

$$m_{30} = \frac{1}{6} \frac{p_k}{v_k^3} p_{30}, m_{40} = \frac{1}{24} \frac{p_k}{v_k^4} p_{40}, \text{ etc. ;}$$

For the definition of  $C_4$  comp. KAMERLINGH ONNES (Arch. Néerl. (2), 5, 670, 1901; Comm. no. 66).

3) The figure is drawn by using the values of  $p_{01}, p_{11}$  etc. which will be calculated in the next section. For clearness I have represented the  $\alpha$ 's in a 5 times larger scale than the  $\beta$ 's.

$bAOB'$  corresponds to KORTEWEG's first boundary<sup>1)</sup>. Outside the parabola  $T_{xpl} > T_k$ , inside  $T_{xpl} < T_k$ .

*The plaitpointpressure.* From form. (60) we derive that  $p_{xpl} >$  or  $< p_k$  as  $\nu_{01} (\beta - \nu_{01} \alpha)^2 >$  or  $< C_4 \nu_{11} \beta$ . The equation of the boundary

$$\nu_{01} (\beta - \nu_{01} \alpha)^2 - C_4 \nu_{11} \beta = 0,$$

is that of a parabola represented in the figure by  $cOBe'$ . Outside the parabola  $p_{xpl} > p_k$ , inside  $< p_k$ .

*The plaitpointvolume.* The manner in which  $v_{xpl}$  depends on  $\alpha$  and  $\beta$  may be derived from form. (61); it is expressed by KEESOM's formula (2c), which I borrow from him in my notations:

$$v_{xpl} = v_k + v_k(\alpha - \beta)x - \frac{(\beta - \nu_{01}\alpha)v_k x}{C_4^2 \nu_{21} \nu_{30}} [\nu_{11}(\beta - \nu_{01}\alpha)^2 - C_4 \nu_{21}(\beta - \nu_{01}\alpha) - 3C_4 \nu_{11}^2 \alpha].$$

Hence the boundary is here:

$$0 = -\nu_{11}(\beta - \nu_{01}\alpha)^2 + C_4 \nu_{21}(\beta - \nu_{01}\alpha)^2 + 3C_4 \nu_{11}^2 \alpha(\beta - \nu_{01}\alpha) + C_4^2 \nu_{11} \nu_{30}(\alpha - \beta).$$

This is a curve of the third degree, like KORTEWEG's third boundary, with which it corresponds in this diagram.

In order to investigate this curve I introduce, following the example of KORTEWEG, a parameter  $z$ , by putting

$$z = \beta - \nu_{01} \alpha.$$

and I find that  $\alpha$  and  $\beta$ , by means of that parameter are expressed thus:

$$\alpha = \frac{z}{N} [-\nu_{11} z^2 + C_4 \nu_{21} z - C_4^2 \nu_{11} \nu_{30}]$$

$$\beta = \frac{z}{N} [-\nu_{01} \nu_{11} z^2 + C_4 \{\nu_{01} \nu_{21} - 3\nu_{11}^2\} z - C_4^2 \nu_{11} \nu_{30}],$$

where

$$N = C_4^2 \nu_{11} \nu_{30} (\nu_{01} - 1) - 3C_4 \nu_{11}^2 z.$$

As  $\alpha$  and  $\beta$  are single valued functions of  $z$ , all lines which are parallel to the straight line  $\beta = \nu_{01} \alpha$  ( $Oa$  of the figure) intersect the curve at one single point at a finite distance.

If we put:

$$z_1 = \frac{C_4 \nu_{30} (\nu_{01} - 1)}{3\nu_{11}},$$

the straight line  $\beta = \nu_{01} \alpha + z_1$ , being a dotted line in the figure ( $CD$ ),

<sup>1)</sup> To avoid mistakes I use here the word boundary, instead of the expression border curve used by KORTEWEG; for in our demonstrations the word border curve has a very special meaning, viz. that of a boundary between stable and unstable states.

<sup>2)</sup> As  $\nu_1$  is also equal to the direction-cosine  $\left(\frac{d\nu}{d\tau}\right)_k$  of the tangent to the reduced vapour tension curve at the critical point, and as it follows from the form of that line that  $\left(\frac{d\nu}{d\tau}\right)_k > 1$ ,  $z_1$  must necessarily be positive.

is an asymptote of the cubic curve. It has two branches, of which the one (*dGE'd'*) situated above the asymptote, is given by values of  $z$ , which are larger than  $z_1$ , the other (*d''OHE'd'''*), below the asymptote for  $z < z_1$ .

$\alpha$  becomes equal to zero not only for  $z = 0$ , but also for two other real values of  $z$ , of which the one is positive, the other negative; I shall call the positive root  $z_2$ , the negative one  $z_3$ . In the same manner  $\beta$  vanishes for  $z = 0$  and also for two other real values of  $z$ , of which again one ( $z_4$ ) is positive, the other ( $z_5$ ) negative. We can prove that always  $z_5 > z_3$ ; for  $z_2$  and  $z_4$ , three cases are possible: both are larger than  $z_1$ , and then  $z_4 > z_2$ , or both are equal to  $z_1$ , or both are smaller than  $z_1$  and then  $z_4 < z_2$ . With the values of the derivatives, to be introduced presently, the order of the roots is:

$$z_4 > z_2 > z_1 > 0 > z_5 > z_3,$$

and hence follows the form of the cubic curve as it is drawn in the figure<sup>1)</sup>.

One can easily see that  $v_{xpl} > v_k$  above the branch  $z > z_1$ , and within the branch  $z < z_1$ , while  $v_{xpl} < v_k$  in the area which lies partly between those two branches and which extends further to the right of both.

*Retrograde condensation* is of the first kind when  $v_{Tpl} < v_{Tr}$ , and of the second when  $v_{Tpl} > v_{Tr}$ . According to form. (41) and (26)  $v_{Tpl} > v_{Tr}$  when  $m_{01}$  and  $m_{01}^2 + RT_k m_{11}$  have the same sign;  $m_{01}^2 + RT_k m_{11}$  is positive outside the parabola *bAOb'* and negative inside, while  $m_{01}$  is positive above the straight line *Oa* and negative below it. Hence we have  $v_{Tpl} > v_{Tr}$  and retrograde condensation of the second kind: 1<sup>st</sup>. inside the parabola *bAOb'* and below the straight line *Oa*, 2<sup>nd</sup>. outside the parabola and above the straight line; at all other points  $v_{Tpl} < v_{Tr}$  and the retrograde condensation is of the first kind.

Here follow the physical characteristics of the fields into which the figure is divided by the boundaries under consideration:

Field 1 :	$T_{xpl} > T_k$ ,	$p_{xpl} > pk$ ,	$v_{xpl} > v_k$ ,	$v_{Tpl} > v_{Tr}$ ,	r. c. II
2 :	$T_{xpl} > T_k$ ,	$p_{xpl} > pk$ ,	$v_{xpl} < v_k$ ,	$v_{Tpl} > v_{Tr}$ ,	r. c. II
3 :	$T_{xpl} > T_k$ ,	$p_{xpl} > pk$ ,	$v_{xpl} < v_k$ ,	$v_{Tpl} < v_{Tr}$ ,	r. c. I
4 :	$T_{xpl} > T_k$ ,	$p_{xpl} > pk$ ,	$v_{xpl} > v_k$ ,	$v_{Tpl} < v_{Tr}$ ,	r. c. I
5 :	$T_{xpl} > T_k$ ,	$p_{xpl} < pk$ ,	$v_{xpl} > v_k$ ,	$v_{Tpl} < v_{Tr}$ ,	r. c. I
6 :	$T_{xpl} < T_k$ ,	$p_{xpl} < pk$ ,	$v_{xpl} > v_k$ ,	$v_{Tpl} > v_{Tr}$ ,	r. c. II
7 :	$T_{xpl} < T_k$ ,	$p_{xpl} < pk$ ,	$v_{xpl} > v_k$ ,	$v_{Tpl} < v_{Tr}$ ,	r. c. I
8 :	$T_{xpl} < T_k$ ,	$p_{xpl} < pk$ ,	$v_{xpl} < v_k$ ,	$v_{Tpl} < v_{Tr}$ ,	r. c. I
9 :	$T_{xpl} < T_k$ ,	$p_{xpl} > pk$ ,	$v_{xpl} < v_k$ ,	$v_{Tpl} < v_{Tr}$ ,	r. c. I.

1) It will be seen that this form agrees entirely with that derived by KORTWEG in the  $\alpha, \gamma$ -diagram from a special equation of state.

It will be seen that the figures 1 and 2 of the plate belonging to the first paper (Comm. 81) refer to points situated in the part on the right of the  $\beta$ -axis of the fields 1 and 2; figs. 3 and 4 to the same fields on the left of the  $\beta$ -axis; figs. 5 and 6 to the fields 7, 8 and 9; figs. 7 and 8 to the part of the fields 3, 4 and 5 lying on the right of the  $\beta$ -axis; figs. 9 and 10 to the same fields on the left of the  $\beta$ -axis; and lastly figs. 11 and 12 to field 6.

In the figure I have marked three points  $P$ ,  $Q$  and  $R$ , of which the first relates to carbon dioxide with a small quantity of hydrogen ( $\alpha = -1,17$ ,  $\beta = -1,62$ ), the second to carbon dioxide with a small quantity of methyl chloride ( $\alpha = 0,378$ ,  $\beta = 0,088$ ) and the third to methylechloride with a small quantity of carbon dioxide ( $\alpha = -0,221$ ,  $\beta = 0,281$ ). From the situation of  $P$ , viz. in field 2, it should follow that  $T_{xpl} > T_k$ , whereas the observations showed that  $T_{xpl} < T_k$ ; this deviation has been pointed out before.<sup>1)</sup> Moreover the situation of  $P$  in field 2 points to a system of isothermals of the mixtures as represented in figs. 1 and 2 of the first paper, while in reality this system of isothermals corresponds to figs. 5 and 6, that is to say to one of the fields 7, 8 or 9. The point  $P$  lies very near the limit of field 9, and hence it is possible that a more accurate determination of  $\alpha$  and  $\beta$  would remove the point  $P$  into field 9 where indeed it should lie according to the plaitpoint constants observed and the character of this field, if at least the law of corresponding states can be applied. The points  $Q$  and  $R$ , so far as we know with certainty, are situated in the right field.<sup>2)</sup>

The straight line  $\beta = r_{01} \alpha$  agrees with KORTEWEG's second boundary. It is determined by the circumstance that along the connodal line  $\left(\frac{dx}{dv}\right)_{pl} = 0$ ; we find from the formulae (37), (41) and (26) that:

$$\left(\frac{dx}{dv}\right)_{pl} = -\frac{2m_{x0}RT_k}{m_{01}^2 + RT_k m_{11}} (v_{T_{pl}} - v_{T_r}) = \frac{m_{01}}{RT_k} v_{T_{pl}},$$

so that  $\left(\frac{dx}{dv}\right)_{pl}$  becomes zero with  $m_{01}$ . Thus above the straight line  $Oa$

$\left(\frac{dx}{dv}\right)_{pl}$  is positive, below it, negative, hence in connection with the

1) Comp. 2<sup>nd</sup> paper, p. 334.

2) It must be remarked that the deviation of the point  $Q$  in consequence of our insufficient knowledge of  $\alpha$  and  $\beta$  would be much less striking than in the case of point  $P$ ; e. g. whether  $Q$  ought to be placed in the neighbouring field 4 or not, could be only concluded from the sign of  $v_{xpl} - v_k$ , but we do not know with certainty what this sign should be for mixtures of carbon dioxide and methylechloride.

preceding it follows that KORTEWEG's eighth case:

$$T_{xpl} < T_k, \quad v_{xpl} < v_k \quad \text{en} \quad \left( \frac{dx}{dv} \right)_{pl} < 0$$

is in general not possible.

A direct proof of this circumstance may easily be given. Because  $m_{01}$  must be negative, I put  $\beta = \nu_{01} \alpha - r^2$ ;  $T_{xpl} < T_k$  requires that

$$(\beta - \nu_{01} \alpha)^2 = C \nu_{11} \alpha - s^2. \quad \text{Hence we may put: } \alpha = \frac{r^4 + s^2}{C_4 \nu_{11}} \quad \text{and}$$

$$v_{xpl} = v_k - v_k (\nu_{01} - 1) \frac{r^4 + s^2}{C_4 \nu_{11}} x + r^2 v_k x + \frac{r^2 v_k x}{C_4^2 \nu_{11} \nu_{30}} [C_4 \nu_{21} r^2 - \nu_{11} (3s^2 + 2r^4)],$$

so that all the terms of  $v_{xpl}$  are positive. Hence we see that, if

$$T_{xpl} < T_k \quad \text{and} \quad \left( \frac{dx}{dv} \right)_{pl} < 0, \quad v_{xpl} < v_k \quad \text{is an impossibility.}$$

#### 18. *The numerical value of the reduced differential quotients.*

To find this numerical value I have first tried to derive it directly from the observations by means of graphical representations; but as I did not succeed in finding more or less reliable values for the higher differential quotients ( $\nu_{21}$ ,  $\nu_{30}$ ,  $\nu_{40}$  etc.) I was obliged to use formulae which satisfactorily represented the observations. Undoubtedly KAMERLINGH ONNES' <sup>1)</sup> developments in series are best fitted for this purpose, although just in the neighbourhood of the critical point, where in our case they have to be applied, they deviate rather much from the observations <sup>2)</sup>. Therefore the values of the derivatives obtained in that way, especially those of the higher orders, can only be considered as approximate.

By means of the temperature co-efficients of reduced virial co-efficients marked by *V. s. 1* <sup>3)</sup> derived from AMAGAT's observations, I find for those virial co-efficients ( $\mathfrak{A}_1$ ,  $\mathfrak{B}_1$ , etc.) and their first derivatives according to the temperature ( $\mathfrak{A}'_1$ ,  $\mathfrak{B}'_1$ , etc.) at the critical point ( $t = 1$ ),

<sup>1)</sup> Proc. Royal Acad. 29 June 1901, Comm. N<sup>o</sup>. 71, and Arch. Néerl. (2), 6, 874, 1901, Comm. N<sup>o</sup>. 74.

<sup>2)</sup> Comp. Arch. Néerl. loc. cit. p. 887. Previously I have given parabolic formulae (Proc. Royal Acad., 31 March 1900, Comm. N<sup>o</sup>. 55 and Arch. Néerl. (2), 6, 650, 1901) which very well represent the observations just in the neighbourhood of the critical point. These formulae, however, do not harmonize with our considerations, because they do not yield finite values for higher derivatives.

<sup>3)</sup> Comm. N<sup>o</sup>. 74, p. 12.

$$\begin{array}{ll}
 \mathfrak{A}_1 = + 366,25 \times 10^{-5} & \mathfrak{A}'_1 = + 366,25 \times 10^{-5} \\
 \mathfrak{B}_1 = - 471,614 \times 10^{-8} & \mathfrak{B}'_1 = + 662,387 \times 10^{-8} \\
 \mathfrak{C}_1 = + 233,300 \times 10^{-11} & \mathfrak{C}'_1 = - 355,774 \times 10^{-11} \\
 \mathfrak{D}_1 = - 360,485 \times 10^{-15} & \mathfrak{D}'_1 = + 789,380 \times 10^{-15} \\
 \mathfrak{E}_1 = + 683,07 \times 10^{-25} & \mathfrak{E}'_1 = + 346,72 \times 10^{-25} \\
 \mathfrak{F}_1 = - 90,14 \times 10^{-32} & \mathfrak{F}'_1 = - 698,82 \times 10^{-32}
 \end{array}$$

If further we put  $\lambda=0,00102$  (calculated from  $T_k=304,45$ ,  $p_k=72,9$  and  $v_k=0,00424$ , we find at the critical point:

$$\begin{array}{l}
 p_{00} = 0,98833, \quad p_{10} = 0,10305, \quad p_{20} = -0,16831, \quad p_{30} = -5,30648. \\
 p_{40} = 75,79292, \quad p_{01} = 7,34410, \quad p_{11} = -9,99986, \quad p_{21} = 27,76382, \text{ etc.}
 \end{array}$$

The values of  $p_{00}$ ,  $p_{10}$  and  $p_{20}$  ought to be equal to 1, 0 and 0 respectively; the tolerably large deviation of the two last derivatives proves that the series used do not represent the shape of the isothermals in the neighbourhood of the critical point so accurately as we might wish<sup>1)</sup>. Hence it follows that the values of the other derivatives calculated here cannot be very precise, and probably this uncertainty increases with the order of the derivative.

I take as approximate values of the reduced differential quotients at the critical point:

$$p_{30} = -5,3, \quad p_{40} = 76, \quad p_{01} = 7,3, \quad p_{11} = -10, \quad p_{21} = 28, \quad \text{while } C_4 = 3,6.^2)$$

According to VAN DER WAALS' original (reduced) equation of state:

$$p = \frac{8t}{3v-1} - \frac{3}{v^2}.$$

we should have

$$p_{30} = -9, \quad p_{40} = 126, \quad p_{01} = 4, \quad p_{11} = -6, \quad p_{21} = 18. \quad C_4 = \frac{8}{3} = 2,7;^3)$$

and according to this modified equation:

$$p = \frac{8t}{3v-1} - \frac{3e^{1-t}}{v^2}:$$

$$p_{30} = -9, \quad p_{40} = 126, \quad p_{01} = 7, \quad p_{11} = -12, \quad p_{21} = 36, \quad C_4 = 2,7.$$

Finally I substitute the numerical values of the derivatives obtained

1) On the cause of that inaccuracy and the possibility of improving upon it a new communication by KAMERLINGH ONNES is to be expected. (Comp. Comm. n<sup>o</sup>. 74, p. 15).

2) KEESOM gives (Comm. n<sup>o</sup>. 75, p. 9 and 10)  $C_4 = 3,45$ ,  $p_{11} = 7$ ,  $p_{11} = -9,3$ .

3) It will be seen that these values agree tolerably well with the former; it is thus not remarkable that so close a resemblance exists between the forms of the boundaries found by KORTEWEG and by me, which indeed is based on VAN DER WAALS' original equation.

above in formulae (9) and (10) and compare the result with the observations.

Equation (9) yields:

$$\frac{1}{2}(v_2 - v_1) = \sqrt[6]{\frac{v_{11}}{v_{30}}(1-t)} = 3,37\sqrt{1-t}$$

and equation (10):

$$\frac{1}{2}(v_2 + v_1) - 1 = -\frac{1}{v_{30}}\left[v_{21} - \frac{3}{5}\frac{v_{11}v_{40}}{v_{30}}\right](1-t) = 10,9(1-t).$$

In order to compare these results with the parabolic formulae of MATHIAS<sup>1)</sup>, formulae must be derived for the reduced densities of the co-existing phases; representing these reduced densities by  $\delta_1$  and  $\delta_2$  I find, according to a transformation employed formerly:<sup>2)</sup>

$$\frac{1}{2}(\delta_1 - \delta_2) = 3,37\sqrt{1-t}$$

$$\frac{1}{2}(\delta_1 + \delta_2) - 1 = (3,37^2 - 10,9)(1-t) = 0,5(1-t).$$

In the last formula, however, the co-efficient 0,5 is somewhat uncertain.

MATHIAS gives for the liquid branch, according to the observations of CALLETET and MATHIAS<sup>3)</sup>,

$$\delta_1 = 1 - 2,47(1-t) + 4,09\sqrt{1-t},$$

and for the vapour branch

$$\delta_2 = 1 + 2,91(1-t) - 3,37\sqrt{1-t}.$$

f From these formulae it would follow that the two branches of the border curve belong to different parabolae. The co-efficient of  $\sqrt{1-t}$  or the vapour branch perfectly agrees with the one found, and the fact that MATHIAS has found a greater value for the same co-efficient in the liquid branch, may clearly be ascribed to the uncertainty of the then existing data on this subject. If we neglect this difference, the formulae of MATHIAS give:

$$\frac{1}{2}(\delta_1 + \delta_2) - 1 = 0,25(1-t),$$

a sufficient agreement with the co-efficient 0,858 later derived by him from AMAGAT's observations. The value 0,5 found above is in good harmony with this.

<sup>1)</sup> Journ. d. Phys., (3), 1, 53, 1892. Ann. d. Toulouse, V.

<sup>2)</sup> Proc. Royal Acad., 27 June 1896; Comm. no. 28, p. 12. More accurately we have

$$q = \frac{1}{v_k + \Phi \pm \varphi} = \frac{1}{v_k} \mp \frac{\varphi}{v_k^2} + \frac{1}{v_k^2}(\varphi^2 - \Phi)$$

<sup>3)</sup> Journ. d. Phys., (3), 2, 5, 1893. Ann. d. Toulouse, VI.

**Physics.** — “*The liquid state and the equation of condition.*” By  
Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of May 30th and June 27th 1903).

It has been repeatedly pointed out that if we keep the values of the quantities  $a$  and  $b$  of the equation of state constant, this equation indicates the course of the phenomena only qualitatively, but in many cases does not yield numerically accurate results. In particular DANIEL BERTHELOT testing the equation of state at the experimental investigations of AMAGAT, has shown that there occur some curves in the net of isothermals, e. g. those indicating the points for which the value of the product  $pv$  is a minimum, and other curves of the same kind, whose general course is correctly predicted by the equation of state, but whose actual shape and position as determined by the experiments of AMAGAT, shows considerable deviations from the course of those curves as it may be derived from the equation of state.

In consequence of this circumstance the quantities  $a$  and  $b$  have been considered as functions of the temperature and volume. Already CLAUSIUS proposed such a modification for the quantity  $a$ ; for carbonic acid he does not put  $a = \text{constant}$ , but he multiplies it with  $\frac{273}{T}$ . Such a modification seems to be required principally with a view to the course of the saturated vapour tension.

From the beginning I myself have clearly pointed out that, though  $a$  may probably be constant, this cannot be the case with the quantity  $b$ . One of the circumstances which I was convinced that I had shown with the highest degree of certainty as well in the theoretic way as by means of the comparison of the experiments of ANDREWS, was that the quantity  $b$  must decrease when the volume decreases. So for carbonic acid I calculated for  $b$  in the gaseous state at 13°1 the value 0,00242 and in the liquid state a value decreasing to 0,001565. But the law of the variability of  $b$  not being known, I have been often obliged to proceed as if  $b$  were constant. In the following pages I will keep to the suppositions assumed by me from the beginning, namely that  $a$  is constant and that  $b$  varies with the volume; and I will show that if we do so, the considerable deviations disappear for the greater part and that it is possible to assume already now a law for the variability of  $b$  with the volume, from which we may calculate in many cases numerically accurate data even for the liquid state at low temperatures.

To that purpose we shall begin with the discussion of the tension of the saturated vapour over liquids at low temperature. From the conditions for coexisting phases of a simple substance, that namely  $p$ ,  $T$  and the thermodynamic potential are the same in both phases, follows:

$$(pv - \int p dv)_1 = (pv - \int p dv)_2$$

or

$$\left( pr - \frac{a}{v} - RT \int \frac{dv}{v-b} \right)_1 = \left( pr - \frac{a}{v} - RT \int \frac{dv}{v-b} \right)_2$$

If we put  $b = \text{constant}$  i. e.  $b$  independent of the volume, then the latter equation assumes the well known form:

$$\left[ pv - \frac{a}{v} - RT \log(v-b) \right]_1 = \left[ pv - \frac{a}{v} - RT \log(v-b) \right]_2$$

Properly speaking this equation is not suitable for the direct calculation of the coexistence pressure; it must be considered to give a relation between the specific volumes and so also between the densities of the coexisting phases. At lower temperatures, however, for which the vapour phase, which we have indicated by means of the index 2, is rare and may be estimated not to deviate noticeably from the gas-laws, the equation becomes suitable for the calculation of the pressure of the saturated vapour. In this case it assumes the following form:

$$pv_1 - \frac{a}{v_1} - RT \log(v_1 - b) - RT = RT \log \frac{p}{RT}$$

We find after successive deductions which are too simple to require special discussion:

$$\begin{aligned} pv_1 - \frac{a}{b} + \frac{a(v_1 - b)}{bv_1} - \left( p + \frac{a}{v_1^2} \right) (v_1 - b) &= RT \log \frac{p(v_1 - b)}{RT} \\ pb - \frac{a}{b} + \frac{a}{v_1^2 b} (v_1 - b)^2 &= RT \log \frac{p}{p + \frac{a}{v_1^2}} \\ pb - \frac{a}{b} + \frac{v_1 - b}{b} [RT - p(v_1 - b)] &= RT \log \frac{p}{p + \frac{a}{v_1^2}} \\ -p \frac{v_1(v_1 - 2b)}{b} - \frac{a}{b} + \frac{v_1 - b}{b} &= \log \frac{p}{p + \frac{a}{v_1^2}} \end{aligned}$$

Undoubtedly  $p$  may be neglected by the side of  $\frac{a}{v_1^2}$ . Even if  $p$  amounts to one Atmosphere, its value is certainly still smaller than 0.0001<sup>th</sup> part of  $\frac{a}{v_1^2}$ . In the same way  $p \frac{v(v-2b)}{b}$  may undoubtedly be neglected by the side of  $\frac{a}{b}$  or  $pv_1(v_1-2b)$  by the side of  $a$  — and this for the same reason, for  $\frac{a}{v_1(2b-v_1)}$  is a quantity of the same order as  $\frac{a}{v_1^2}$ .

So the equation may be simplified to:

$$\log \frac{p}{\frac{a}{v_1^2}} = -\frac{\frac{a}{b}}{RT} + \frac{v_1 - b}{b} \dots \dots \dots (1)$$

For the limiting case, when  $v_1$  may be equated to  $b$ , we get:

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

If we introduce the critical data, namely:

$$pv = \frac{1}{27} \frac{a}{b^2} \text{ and } RT_k = \frac{8}{27} \frac{a}{b}$$

then we get the following equation for the calculation of  $p$ :

$$-\log \frac{p}{p_k} = \frac{27}{8} \frac{T_k}{T} - \log 27$$

or, as  $\log 27$  is equal to 3,3 and may therefore be nearly equated to  $\frac{27}{8}$  we get with a high degree of approximation:

$$-\log \frac{p}{p_k} = 3,375 \frac{T_k - T}{T}$$

This last equation is nearly equal to that derived by prof. KAMERLINGH ONNES by means of a graphical method from the equation of state with  $a$  and  $b$  constant, namely:

$$-\log \frac{p}{p_k} = 3,4 \left( \frac{T_k - T}{T} \right)$$

KAMERLINGH ONNES found this equation to hold in approximation up to the critical temperature, here we could only derive it for low

1) Arch. Néerl. Livre Jub. dédié à H. A. LORENTZ. p. 676.

temperatures. If in equation (1) we do not immediately introduce  $v_1 = b$ , we may write it as follows:

$$\log \frac{p}{\frac{a}{b^2} \left( \frac{v_1}{b} \right)^2} = -\frac{\frac{a}{b}}{RT} + \frac{v_1 - b}{b}$$

or

$$\log \frac{p}{a} = -\frac{\frac{a}{b}}{RT} + \frac{v_1 - b}{b} - 2 \log \frac{v_1}{b}.$$

For values of  $v_1$  only slightly greater than  $b$  we may write  $\frac{v_1 - b}{b}$  for  $\log \frac{v_1}{b}$ . So we get:

$$-\log \frac{p}{p_k} = \frac{27}{8} \frac{T_k}{T} + \frac{v_1 - b}{b} - \log 27.$$

The value of  $\frac{v_1 - b}{b}$  varies with the temperature and starts with the value zero for  $T = 0^\circ$ . It may be calculated from:

$$\frac{a}{v_1^2} (v_1 - b) = RT.$$

This last equation may be written as follows:

$$\frac{8}{27} \frac{T}{T_k} = \frac{\left( \frac{v_1}{b} - 1 \right)}{\left( \frac{v_1}{b} \right)^2}.$$

With  $\frac{T}{T_k} = \frac{15}{32}$  we find for  $\frac{v_1 - b}{b}$  the value  $\frac{1}{5}$  and with  $\frac{T}{T_k} = 0,54$  the value  $\frac{1}{4}$ . With  $\frac{T}{T_k} = \frac{1}{2}$  the value of  $\frac{v_1 - b}{b}$  is equal to 0,2125.

The quantity  $\frac{v_1 - b}{b}$  varying with the temperature, the term  $\frac{27}{8} \frac{T}{T_k}$  does not represent the total variation of  $\beta$  with the temperature, but the difference is small. We might calculate the value of  $\frac{T}{p} \frac{dp}{dT}$  from the above equation, but it is simpler to calculate this quantity from the following equation:

$$T \left( \frac{\partial p}{\partial T} \right)_v - p = \left( \frac{\partial \varepsilon}{\partial v} \right)_T$$

For coexisting phases this equation becomes:

$$T \frac{dp}{dT} - p = \frac{\varepsilon_2 - \varepsilon_1}{v_2 - v_1}$$

or

$$T \frac{dp}{dT} - p = \frac{a}{v_2 - v_1} = \frac{a}{v_1 v_2} \dots \dots \dots (2)$$

For low temperatures this yields:

$$\frac{T}{p} \frac{dp}{dT} - 1 = \frac{a}{RT} = \frac{a}{RT} - \frac{a(v_1 - b)}{RT v_1 b}$$

or

$$\frac{T}{p} \frac{dp}{dT} - 1 = \frac{a}{RT} - \frac{v_1}{b}$$

or

$$\frac{T}{p} \frac{dp}{dT} = \frac{27}{8} \frac{T_k}{T} - \frac{v_1 - b}{b}$$

For  $T = T_k$  equation (2) yields:

$$\left( \frac{T}{p} \frac{dp}{dT} \right)_k = 4.$$

For the highest temperature, therefore, at which the pressure curve occurs, the coefficient with which  $\frac{T_k}{T}$  must be multiplied in order to yield the value of  $\frac{T}{p} \frac{dp}{dT}$ , does not differ much from that for the lowest temperature at which the liquid may exist without solidification.

Here we have one of the striking instances, how the equation of state with constant  $a$  and  $b$  may represent the general course of a quantity just as it is found in reality, though the numerical value differs considerably. For the real course of the vapour tension is at least in approximation represented by the formula:

$$- \log \frac{p}{p_k} = f \frac{T_k - T}{T},$$

but the value of  $f$  is not 4 or somewhat less — but for a great many substances a value is found which does not differ much from 7.

Before discussing this point further, we shall calculate some other quantities whose values for the liquid state for low temperatures follow from the equation of state when we keep  $a$  and  $b$  constant.

Let us take again  $p$  to be so small that we may write

$$\frac{a}{v^2}(v-b) = RT.$$

From this we may deduce:

$$1 = \left( \frac{T}{v} \frac{dv}{dT} \right)_{p=0} \times \left\{ \frac{v}{v-b} - 2 \right\} \dots \dots \dots (3)$$

For  $\frac{T}{T_k} = 0,585$  (Ether at  $0^\circ$ )  $\frac{v}{v-b}$  is equal to 4,7 as appears from :

$$\frac{8}{27} \frac{T}{T_k} = \frac{\left( \frac{v}{b} - 1 \right)}{\left( \frac{v}{b} \right)^2}.$$

With this value  $\frac{v}{v-b} = 4,7$  we find:

$$\frac{T}{v} \left( \frac{dv}{dT} \right)_{p=0} = \frac{1}{2,7}.$$

So we find for the coefficient of dilatation under low pressure and at this temperature which is so low that we may neglect the pressure, the value:

$$\frac{1}{v} \left( \frac{dv}{dT} \right)_{p=0} = \frac{0,00367}{2,7} = 0,00136.$$

Comparing this value with that which the experiment has yielded and which we may put at 0,001513, we see that it may be used at least as an approximated value.

The above equation (3) yields for  $\frac{1}{v} \left( \frac{dv}{dT} \right)_{p=0}$  with  $v = 2b$  an infinite value and so  $\frac{T}{T_k} = \frac{27}{32}$ . This quite agrees with the circumstance that the isothermal for  $\frac{T}{T_k} = \frac{27}{32}$  touches the  $V$ -axis and it warns us that equation (3) cannot yield any but approximated values for much lower values of  $T$ .

For the coefficient of compressibility  $\beta$  namely  $-\left( \frac{dv}{v dp} \right)_T$  in that same liquid state we find

$$-v_1 \left( \frac{dp}{dv_1} \right)_T = \frac{RTv_1}{(v_1-b)^2} - \frac{2a}{v_1^2} = \frac{a}{v_1^2} \left( \frac{v_1}{v_1-b} - 2 \right)$$

or

$$\frac{1}{\beta} = 27 p_k \left( \frac{b}{v_1} \right)^2 \left( \frac{v_1}{v_1-b} - 2 \right).$$

With the aid of the above data and putting  $\mu_k=37,5$  atmospheres we find:

$$\beta = 0.0006 \text{ (nearly).}$$

The experiment has yielded no more than about 0,00016 for this value. So we have found it so many times too large, that for this quantity the equation of state with constant  $a$  and  $b$  cannot be considered to hold good even in approximation.

From the well known equation:

$$\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_T = -1$$

follows

$$\frac{T}{v} \left(\frac{\partial v}{\partial T}\right)_p \left(-v \frac{\partial p}{\partial v T}\right) = T \left(\frac{\partial p}{\partial T}\right)_v$$

and therefore

$$\frac{T}{v} \left(\frac{dv}{dT}\right)_p \times \frac{1}{\beta} = \frac{a}{v^2} \text{ 1)}$$

With the values mentioned above and yielded by the experiment we should therefore have for ether at  $0^\circ$ :

$$\frac{273 \times 0,001513}{0,00016} = 27 \times 37,5 \left(\frac{b}{v}\right)^2$$

or

$$2,5 = \left(\frac{b}{v}\right)^2.$$

According to this equation  $v$  should be smaller than  $b$  which would be absurd, if  $b$  does not vary with the volume.

If we calculate the value of  $b$  from  $\frac{RT_k}{8p_k}$  then we find for ether  $b=0,0057$  circa; in reality the liquid volume appears to be smaller than  $b$ . Dividing namely the molecular liquid volume by the normal molecular gas volume we find about 0,0047<sup>2)</sup>. From this appears convincingly that the variability of  $b$  exists in reality and that therefore an equation of state in which this variability is not taken into account, cannot possibly yield the data of the liquid state.

Let us return to the equation:

$$-\log \frac{p_k}{p} = f \frac{T_k - T}{T},$$

which holds good at least approximately, as is confirmed by the experiments, if we take for  $f$  a value which is about twice as great as would follow from the equation of state if we keep  $a$  and  $b$  con-

1) Continuität 2nd Edition, p. 171.

2) Continuität 2nd Edition, p. 172.

stant. What modification must the equation of state be subjected to in order to account for this twice greater value? CLAUSIUS answered this question by supposing  $a$  to be a function of the temperature e. g. by substituting  $a \frac{273}{T}$  for it.

When we consider the question superficially, the difficulty seems to be solved. But it is only seemingly so. At  $T = T_k$  this modification really causes  $f$  to assume the value 7 — but this supposition has consequences which for lower temperatures are contrary to the experiment. If we calculate the value of

$$T \frac{dp}{dT} - p = \frac{\epsilon_2 - \epsilon_1}{v_2 - v_1},$$

as on page 4 and if we take into account that  $\epsilon = -2 \frac{a}{v} \frac{273}{T}$  we find

$$\frac{Tdp}{pdT} - 1 = \frac{2 \frac{a}{v_1} \frac{273}{T}}{RT}.$$

For lower temperatures we will put  $v_1 = b$  and we deduce approximately :

$$\frac{Tdp}{pdT} = 2 \frac{a}{b} \frac{273}{RT^2}$$

or <sup>1)</sup>

$$\frac{T}{p} \frac{dp}{dT} = 2 \times \frac{27}{8} \left( \frac{T_k}{T} \right)^2.$$

For  $\frac{T}{T_k} = \frac{1}{2}$  we find then for  $\frac{T}{p} \frac{dp}{dT}$  a value which is not twice as great as that which follows from a constant value of  $a$ , but a value which is four times as great.

The equation :

$$\left[ pv - \int pdv \right]_1 = \left[ pv = \int pdv \right]_2$$

yields for this value of  $a$  :

$$- \log \frac{p}{pk} = 2 \times \frac{27}{8} \left( \frac{T_k}{T} \right)^2 - \log \left( 27 \frac{T_k}{T} \right) + 1.$$

In order to agree with  $f' \left( \frac{T_k}{T} - 1 \right)$  the positive term of the right-hand member of this equation should have the form  $2 \times \frac{27}{8} \frac{T_k}{T}$ ; and the negative term should not be  $\log 2 \times 27$ , but  $\log 27^2$ .

<sup>1)</sup> Continuität, p. 171.

The imperfect agreement between the real course of the vapour tension and that derived from the equation of state with  $a$  and  $b$  constant, has induced us to assume that  $a$  is a function of the temperature. It appears however that this agreement is not satisfactorily established by the modification proposed by CLAUDE. It will therefore be of no use to proceed further in this way — specially because this modification in itself is certainly insufficient to account for the fact that liquid volumes occur which are even smaller than  $b$ .

If we had not supposed  $a$  to increase so quickly with decreasing temperature as agrees with  $a \frac{T_k}{T}$ ; if we had chosen  $ae^{1-\frac{T}{T_k}}$  for instance, then the greater part of the above difficulties would have vanished.

We should then have found:

$$\frac{T}{p} \frac{dp}{dT} - 1 = \left( 1 + \frac{T}{T_k} \right) \frac{ae^{1-\frac{T}{T_k}}}{RTv_1}.$$

The expression  $\left( 1 + \frac{T}{T_k} \right) e^{1-\frac{T}{T_k}}$  is equal to 2 at  $T = T_k$  and at  $T = 0$  it would have increased to  $e = 2,728$  etc.; so the increase is relatively small. But the term which should be found equal to  $\log 27^2$ , would also have remained far below the required value. For this reason it seems desirable to me to inquire, in how far the variability of  $b$  alone can account for the course of the vapour tension.

As I dared not expect that the variability of  $b$  could explain the course of the vapour tension as it is found experimentally, and in any case not being able to calculate this variability, I have often looked for other causes, which might increase the value of the factor  $f'$  from  $\frac{27}{8}$  to about twice that value. The quantity  $\frac{a}{v}$  representing the amount with which the energy of the substance in rare gaseous condition surpasses that of the same substance in liquid condition, and this quantity seeming — from the value of  $\frac{Tdp}{pdT}$  — to be only half of what it should be, I have thought that the transformation of liquid into vapour ought perhaps to be regarded as to consist of two transformations. These two transformations would be: that of liquid into vapour and that of complex molecules into simple gasmolecules. If this really happened then the liquid state would essentially differ from the gaseous state even for substances which we consider to be

normal. We should then have reason to speak of "molécules liquidogènes" and "molécules gazogènes". It would then, however, be required that the following equalities happened to be satisfied. In the first place the two transformations would require the same amount of energy; and in the second place the number of "molécules liquidogènes" in the liquid state <sup>1)</sup> at every temperature would have to be proportional with the value of  $\frac{p(v_2 - v_1)}{T}$ . The following equation would then hold:

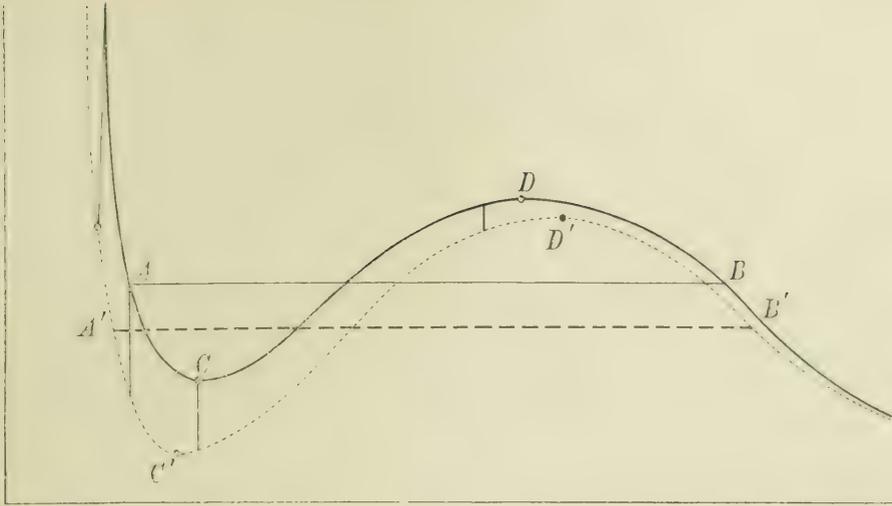
$$\frac{Tdp}{pdT} - 1 = \frac{\frac{a}{v_1} - \frac{a}{v_2} + (x_2 - x_1)E}{p(v_2 - v_1)} = \frac{a}{v_1 v_2 p} + \frac{(x_2 - x_1)\varepsilon}{p(v_2 - v_1)}$$

Not succeeding in deducing this course of the amount of the liquidogène molecules from the thermodynamic rules and in accounting for the above mentioned accidental equalities I have relinquished this idea, the more so as this supposition is unable to explain the fact that the liquid volume can decrease below  $b$ .

If we ask what kind of modification is required in the equation of state with constant  $a$  and  $b$  in order to obtain a smaller vapour tension, we may answer that question as follows. Every modification which lowers the pression with an amount which is larger according as the volume is smaller, satisfies the requirement mentioned. In the following figure the traced curve represents the isothermal for constant  $a$  and  $b$ ; the straight line  $AB$ , which has been constructed according to the well known rule indicates the coexisting phases, and the points  $C$  and  $D$  represent the phases with minimum pressure and maximum pressure. The dotted curve has been constructed in such a way that for very large volumes it coincides sensibly with the traced curve, but for smaller volumes it lies lower, and the distance is the greater according as the volume is smaller. Then the point  $D$  has shifted towards the right and the point  $C'$  towards the left. For in the point exactly below  $D$  as well as in the point exactly below  $C$  the value of  $\frac{dp}{dv}$  for the dotted curve is positive;

these points lie therefore on the unstable part of the modified isothermal and the limits of the unstable region are farther apart. But it is also evident — and this is of primary interest — that if for the modified isothermal we trace again the straight line of the coexisting phases according to the well know rule, this line will lie lower than the line  $AB$ . The area of the figure above  $AB$

<sup>1)</sup> Diminished with that number in the gaseous state.



has decreased, that of the figure below  $AB$  has increased in consequence of the modification. The line  $A'B'$  must therefore be traced noticeably lower in order to get again equal areas.  $B'$  will of course lie on the right of  $B$ , and we may also expect that  $A'$  will lie on the left of  $A$ .

We have, however, put the question in too general terms; for our purpose it should have been put as follows: what modification in the quantities  $a$  and  $b$  makes the vapour pressure at a temperature which is an equal fraction of  $T_k$ , decrease below the amount which we find for it, keeping  $a$  and  $b$  constant — and it would even be still more accurate not to speak of the absolute value of the pressure, but of the fraction  $\frac{p}{p_k}$ . The modifications in  $a$  and  $b$  should then be such, — if we base our considerations on the preceding figure — that in consequence of the modifications themselves the values of  $T_k$  and  $p_k$  either do not change at all or very slightly.

If we make  $a$  a function of the temperature we have to compare the following two equations:

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

and

$$p = \frac{KT}{v-b} - \frac{aT_k}{Tv^2}$$

Both equations yield  $RT_k = \frac{8}{27} \frac{a}{b}$  and  $p_k = \frac{1}{27} \frac{a}{b^2}$  i. e. the same values for  $T_k$  and  $p_k$  if  $a$  and  $b$  have the same values in both

equations. The value of  $p$  — the values of  $T$  and  $v$  being the same for both curves — for the modified isothermal is smaller than that for the isothermal with constant  $a$  and  $b$ , and the difference is greater according as the volume is smaller. According to the figure discussed  $\frac{p}{p_k}$  — the value of  $\frac{T}{T_k}$  being the same for both curves — will therefore have a smaller value for the modified isothermal than for the unmodified one. A value of  $a$  increasing with decreasing value of  $v$  would have the same effect. But I have not discussed a modification of this kind, at least not elaborately, because I had concluded already before (see “*Livre Jub. dédié à LORENTZ*” p. 407) that the value of the coefficient of compressibility in liquid state can only be explained by assuming a molecular pressure of the form  $\frac{a}{v^2}$ . The supposition of complex molecules in the liquid state would involve a modification of the kinetic pressure to  $\frac{RT}{v-b} \varphi(vT)$ , where  $\varphi(v, T)$  must increase with decreasing value of  $v$ . Also this supposition would lead to a smaller value of  $\frac{p}{p_k}$  for the same value of  $\frac{T}{T_k}$ . This is namely certainly true, if the greater complexity has disappeared in the critical state, and if therefore the values of  $T_k$  and  $p_k$  are unmodified; probably it will also be the case if still some complex molecules occur even in the critical state. But whether this is so or not can only be settled by a direct closer investigation, and for this case the property of the drawn figure alone is not decisive. I have, however, already shown above, that we cannot regard this circumstance as the probable cause of the considerable difference between the real value of the vapour pressure and that calculated from the equation of state with constant  $a$  and  $b$ . So we have no choice but to return to my original point of view of 30 years ago and to suppose  $b$  to be variable, so that the value of  $b$  decreases with decreasing volume. It is clear that a variability of this kind causes the kinetic pressure  $\frac{RT}{v-b}$  to be smaller than we should find it with constant  $b$ , and the more so according as  $b$  is smaller. Moreover it is possible in this way to account for the fact, that liquid volumes occur smaller than the value which  $b$  has for very large volumes and which I shall henceforth denote by  $b_g$ . Or I may more accurately say that I do not return to that point of view, for properly speaking I have never left it. As the law of the variability was not known, I could

not develop the consequences of this decreasing value of  $b$  — but it appears already in my paper on “The equation of state and the theory of cyclic motions” and in the paper in the “*Livre Jub. dédié à LORENTZ*” quoted above that I still regarded the question from the same point of view.

My first supposition concerning the cause of the decrease of  $b$  with the volume was not that the smaller value of  $b$  corresponded to smaller volume of the molecules.  $b_g$  being equal to four times the molecular volume, I supposed smaller values of  $b$  to be lower multiples of this volume. In this way of considering the question the decrease of  $b$  does not indicate a real decrease of the volume of the molecules. We will therefore call it a quasi-decrease.

It can scarcely be doubted that such a quasi-decrease of the volume of the molecules exists. In his “*Vorlesungen*” BOLTZMANN started from the fundamental supposition that the state of equilibrium i.e. the state of maximum-entropy is at the same time the “most probable state”; in doing which he was obliged to take into account the chance that two distance spheres partially coincide. And comparing the expression which he found in this way for the maximum-entropy with the expression  $R \int \frac{dv}{v-b}$  (i. e. the entropy in the state of equilibrium according to the equation of state) it was possible for him to determine the values of some of the coefficients of the expression:

$$b = b_g \left\{ 1 - \alpha \left( \frac{b_g}{v} \right) + \beta \left( \frac{b_g}{v} \right)^2 \dots \right\}.$$

This method is indirect. I myself had tried to find these coefficients by investigating directly the influence of the coincidence of the distance spheres on the value of the pressure. According to these two different methods different values for the coefficients were found. My son has afterwards pointed out (see these Proceedings 1902) that also according to the direct method a value of  $\alpha$  equal to that calculated by BOLTZMANN is found, if we form another conception of the influence on the pressure than I had formed and since then I am inclined to adopt the coefficients calculated according to the method of BOLTZMANN as accurate.

But these values apply only to spherical molecules and only in the case of monatomic gases we may suppose molecules with such a shape. It is not impossible that for complex molecules these coefficients will be found to be much smaller. Moreover for the determination of  $\int \frac{dv}{v-b}$  knowledge of all the coefficients is required — and

we cannot expect that the calculations required for this purpose will soon be performed. Even the determination of  $\beta$  required an enormous amount of work — compare the calculations of VAN LAAR.

For complex molecules another reason is possible for decrease of  $b$  with decreasing volume. The molecules might really become smaller under high kinetic pressure i.e. in the case of high density. If the atoms move within the molecule — and we can hardly doubt that they do so — they require free space. And it is highly probable, we may even say it is certain, that this space will diminish when the pressure which they exercise on one another, is increased. The mechanism of the molecules however being totally unknown it is impossible to decide a priori whether this decrease of the volume of the molecules will have a noticeable effect on the course of the isothermal. In my application of the theory of cyclic motions on the equation of state I have tried to give the formula which would represent such a real decrease of the volume of the molecules with diminishing volume. VAN LAAR has tested this formula to AMAGAT'S observations on hydrogen, — and though new difficulties have arisen, the agreement is such that we may use the given formula at any rate as an approximated formula for the dependency of  $b$  on  $v$ . I will apply the formula, which may have a different form in different cases, in the following form :

$$\frac{b-b_0}{v-b} = 1 - \left( \frac{b-b_0}{b_g-b_0} \right)^2 \cdot \dots \dots \dots (4)$$

The symbols  $b_g$  and  $b_0$  in this formula denote the limiting values for  $b$ , the first for infinitely large volume, the second for the smallest volume in which the substance can be contained. For more particulars I refer to my paper on "The equation of state and the theory of cyclic motions." VAN LAAR concluded from his investigation that agreement is only to be obtained if  $b_0$  decreases with  $T$ , a result which I myself had already obtained applying the formula for carbonic acid (Arch. Néerl. Serie II, Tome IV, pag. 267). If this is really the case and if it appears to be also true after we have modified the formula in some way or other compatible with the manner in which it is derived, then the following difference exists between the course of  $b$  with  $v$  when ascribed to a quasi-diminishing and when ascribed to a real diminishing of the volume of the molecules: in the first case  $b$  is independent of  $T$ , in the second case however it does depend on  $T$ . The fact that  $\left( \frac{dp}{dt} \right)_v$  is not perfectly constant seems to plead for the latter supposition.

For the present, however, I leave these questions and difficulties out of consideration, and I confine myself to showing that a formula of the form (4) can really make the considerable differences disappear which we have met with till now. The more so as this formula appears to be adapted for the derivation of general consequences, which follow from the decrease of  $b$  with  $v$ . I leave therefore a possible dependency of  $b_0$  on  $T$  out of consideration. Moreover in applying the formula I will suppose  $b_y = 2 b_0$ . I choose one — in some respect arbitrarily — from all the forms which I have found to be possible (compare also my paper in the Arch. Néerl. “Livre Jub. dédié à Bosscha”). The numerous calculations required in order to investigate in how far modifications are necessary and possible in order to make the agreement with the experiments more perfect, may perhaps be performed later.

A. *The tension of the saturated vapour.*

Let us begin with the calculation of the pressure of the saturated vapour at low temperatures and let us to that purpose write the equation expressing that the thermo-dynamic potential has the same value in coexisting phases, in the following form:

$$\left[ pv - \frac{a}{v} - RT \int \frac{d(v-b)}{v-b} - RT \int \frac{db}{v-b} \right]_1 = \left[ \dots \dots \dots \right]_2$$

of

$$\left[ pv - \frac{a}{v} - RT \log(v-b) - RT \int \frac{db}{v-b} \right]_1 = \left[ \dots \dots \dots \right]_2$$

In my paper “De kinetische beteekenis der thermodynamische potentiaal” I have already pointed out the signification of the term  $RT \int \frac{db}{v-b}$ ; it represents namely the amount of work performed by the kinetic pressure on the molecule when this passes in a reversible way from the condition of the first phase into that of the second phase and when its volume is therefore enlarged either fictitiously or as we now take it to be, really. We may calculate this term if we assume the chosen form for  $b$  and this is one of the reasons why I adhere to the idea of a real increase of the molecular volume. But though its value may depend upon the particular form which we have assumed for  $b$ , it will certainly have a positive value for every law of variability of  $b$  with  $v$  which we may choose.

Let us for the calculation of  $\int \frac{db}{v-b}$  denote  $\frac{b-b_0}{b_y-b_0}$  by  $z$ , then we

have  $db = (b_g - b_0) dz$  and according to the form of formula (4) chosen for  $b$ :

$$\frac{b_g - b_0}{v - b} = \frac{1 - z^2}{z}$$

in consequence of which  $\int \frac{db}{v - b}$  passes into  $\int \frac{1 - z^2}{z} dz = \log z - \frac{1}{2} z^2$ .

Substituting into the expression for the thermodynamic potential we get:

$$pv - \frac{a}{v} - RT \log(v - b) - RT \log \frac{b - b_0}{b_g - b_0} - \frac{1}{2} RT \left( \frac{b - b_0}{b_g - b_0} \right)^2$$

If we suppose the temperature to be low, the second phase is a rare gas phase and we have:

$$pv = RT, \log(v - b) = -\log \frac{p}{RT} \text{ and } \frac{b - b_0}{b_g - b_0} = 1.$$

In consequence of this we get:

$$pv_1 - \frac{a}{v_1} - RT \log(v_1 - b_1) - RT \log \frac{b_1 - b_0}{b_g - b_0} - \frac{1}{2} RT \left( \frac{b_1 - b_0}{b_g - b_0} \right)^2 = RT + RT \log \frac{p}{RT} - \frac{1}{2} RT$$

or

$$pv_1 - \frac{a}{v_1} - RT - RT \log \frac{b_1 - b_0}{b_g - b_0} + \frac{1}{2} RT \frac{b_1 - b_0}{v_1 - b_1} = RT \log \frac{p(v_1 - b_1)}{RT}$$

or

$$pv_1 - \frac{a}{b_1} + RT \frac{v_1 - b_1}{b_1} - \frac{p(v_1 - b_1)^2}{b_1} - RT \log \frac{b_1 - b_0}{b_g - b_0} + \frac{1}{2} RT \frac{b_1 - b_0}{v_1 - b_1} = RT \log \frac{p}{p + \frac{a}{v_1^2}}$$

As yet we have not applied any approximation for the liquid condition.

If in the first member we collect the terms containing  $p$ , we may write them as follows:

$$-p \frac{v_1^2 - 2b_1 v_1}{b_1}$$

The value of  $v_1$  in the liquid condition being only slightly larger than  $2b_1$ , the value of this expression remains below  $p b_1$  and it may certainly be neglected; if in the second member we neglect also  $p$  compared with  $\frac{a}{v_1^2}$ , then we may write the equation for the calculation of the vapour pressure at low temperatures as follows:

$$\log \frac{p}{a} = -\frac{b_1}{RT} + \frac{v_1 - b_1}{b_1} - \log \frac{b_1 - b_0}{b_g - b_0} + \frac{1}{2} \frac{b_1 - b_0}{v_1 - b_1} \quad (5)$$

In order to draw attention to the principle circumstances, we shall assume for the present that the following equations also hold in the case that  $b$  is variable :

$$RT_k = \frac{8}{27} \frac{a}{b_g}$$

and

$$p_k = \frac{1}{27} \frac{a}{b_g^2}$$

Equation (5) may then be written in this form :

$$\log \frac{p}{27 p_k \left(\frac{b_g}{v_1}\right)^2} = -\frac{27}{8} \frac{T_k b_g}{T b_1} + \frac{v_1 - b_1}{b_1} - \log \frac{b_1 - b_0}{b_g - b_0} + \frac{1}{2} \frac{b_1 - b_0}{v_1 - b_1}.$$

A comparison of this equation with :

$$- \log \frac{p}{p_k} = f \left( \frac{T_k}{T} - 1 \right).$$

shows that it is possible to satisfy the condition that the coefficient of  $\frac{T_k}{T}$  approaches to 7 by equating  $\frac{b_g}{b_1}$  to 2, i.e. by assuming that the molecules in volumes equal to the volume of liquids at low temperatures are only half as large as those in the gaseous condition. But the agreement in the value of the coefficient of  $\frac{T_k}{T}$  does not suffice for establishing agreement between the calculated value and that of the formula which at low temperatures is followed by the vapour tension, though it be only in large features. For this purpose it is required that

$$\left[ \log 27 \left(\frac{b_g}{v_1}\right)^2 \frac{b_g - b_0}{b_1 - b_0} \right] + \frac{1}{2} \frac{b_1 - b_0}{v_1 - b_1} + \frac{v_1 - b_1}{b_1}$$

differs only slightly from 7.

We must return to the equation of state in order to be able to determine the value of this expression, and we must investigate its consequences for the case that  $\rho$  may be neglected compared with

$\frac{a}{v^2}$ . So we must return to :

$$\frac{a}{v_1^2} (v_1 - b_1) = RT = \frac{8}{27} \frac{a}{b_g} \frac{T}{T_k}$$

If we express  $b_1$  and  $v_1$  in the quantity  $z$ , we get :

$$b_1 = b_0 + z(b_g - b_0)$$

and

$$v_1 - b_1 = \frac{1 - z^2}{z} (b_g - b_0)$$

or

$$r_1 = b_0 + \left( z + \frac{1-z^2}{z} \right) (b_g - b_0)$$

Substituting these values and putting  $b_g = n b_0$  we get the equation :

$$\frac{8}{27} \frac{T}{T_k} = \frac{n(n-1) \frac{z}{1-z^2}}{\left\{ 1 + \left( z + \frac{z}{1-z^2} \right) (n-1) \right\}^2}$$

If we put $n = 2$ , then we get $z = \frac{1}{4}$	for	$\frac{T}{T_k} = 0,8$
$z = \frac{1}{5}$	,,	$\frac{T}{T_k} = 0,7$
$z = \frac{1}{6}$	,,	$\frac{T}{T_k} = 0,65$
$z = \frac{1}{7}$	,,	$\frac{T}{T_k} = 0,615$ .

For very small values of  $z$  we may neglect  $z^2$  compared to unity and we may calculate the value of  $z$  from the approximated equation:

$$\frac{8}{27} \frac{T}{T_k} = \frac{2z}{(1+2z)^2},$$

which equation yields the value of  $z = \frac{1}{9}$  for  $\frac{T}{T_k} = \frac{1}{2}$ . For such

small values of  $z$  we have :  $\frac{b_1 - b_0}{v_1 - b_1} = 1$ ,  $\frac{r_1 - b_1}{b_1} = \frac{z}{1+z}$  and  $\frac{v_1}{b_1} = \frac{1+2z}{1+z}$ .

We will assume that for all temperatures below  $0,6 T_k$  the vapour phase may be considered to have a sufficient degree of rarefaction for following the gaslaws; therefore we may assume  $z$  to have a

value below  $\frac{1}{8}$ . If we choose  $z = \frac{1}{8}$ , then we find for  $\left( \frac{b_g}{v_1} \right)^2$  the

value  $4 \left( \frac{b_g}{v_1} \right)^2 = 4 \left( \frac{1}{1+2z} \right)$  or  $\frac{4 \times 16}{25} = 2,56$ . With this value we have :

$$\log 27 \left( \frac{b_g}{v_1} \right)^2 \frac{b_g - b_0}{b_1 - b_0} + \frac{1}{2} \frac{b_1 - b_0}{v_1 - b_1} + \frac{v_1 - b_1}{b_1} = \log 27 \times 20,5 + \frac{1}{2} + 0,11.$$

It is true that this value is smaller than  $\log 27^2$ , but it approaches sufficiently to that value. The fact that it is smaller than  $\log 27^2$  is in perfect agreement with the circumstance that for the quantity  $f$  in

the formula  $-\log \frac{p}{p_k} = f \frac{T_k - T}{T}$  according to the experiments at low

temperatures a higher value must be chosen in order to establish agreement. For a higher value of  $f'$  yields the same result as a not higher value of  $f'$  in  $f' \frac{T_k}{T}$ , from which a smaller quantity is subtracted.

It might appear that the dependency of  $\rho$  on  $T$  is strongly increased by the difference between the values of  $z$  for different temperatures. The following relation however always holds good if  $b$  is independent of  $T$ :

$$\frac{T dp}{p dT} - 1 = \frac{a}{RT}$$

and therefore (see p. 127)

$$\frac{T dp}{p dT} = \frac{a}{RT} - \frac{v_1 - b_1}{b_1}$$

or

$$\frac{T dp}{p dT} = \frac{27 T_k b_g}{8 T b_1} - \frac{v_1 - b_1}{b_1}$$

In the supposition made here, this is equal to:

$$\frac{T dp}{p dT} = \frac{27 T_k}{4 T} \frac{z}{1+z} - \frac{z}{1+z}$$

which expression does not vary much with  $z$ , if  $z$  remains small.

Yet we find the value of  $\frac{T dp}{p dT}$  at low temperatures for most substances to be somewhat higher than is indicated by this formula. We should in fact have found a higher value if we had assumed  $b_g > 2b_0$ . If therefore we had only to deal with the formula for the vapour tension, then it would be rational to investigate the consequences of the suppositions:  $n = 2 \frac{1}{4}$  or  $n = 2 \frac{1}{2}$ . Other experimental quantities however follow less perfectly the formula chosen for  $b$ , if we give  $n$  these values. Therefore I will confine myself to the investigation of the consequences of the equation chosen for  $b$  with  $n = 2$ .

I think the following theoretical observation to be of some importance, even if we disregard the question whether we have established a perfect, numerically accurate agreement with the experiments, by assuming the quantity  $b$  only to be variable, and even this variability to be independent of  $T$ . The pressures in two coexisting phases which lie at a great distance from the critical conditions satisfy, if

we suppose the volume of the molecules to be invariable, the following approximated equation

$$\log \frac{p}{M} = - \frac{\frac{a}{b}}{RT}.$$

In this formula  $M$  denotes the pressure of the liquid phase i. e. the molecular pressure, and  $\frac{a}{b}$  the heat required for the transformation.

The following approximated equation holds for molecules of variable volume:

$$\log \frac{p}{Mk} = - \frac{\frac{a}{b_1}}{RT},$$

where again  $\frac{a}{b_1}$  denotes the heat required for the transformation, which is greater if the molecules in the liquid phase are smaller, as well in the case that this diminishing of the volume is real, as in the case that it is only fictitious. Again the molecular pressure is also higher. But the molecular pressure is now provided with the factor  $K$ . If it is a real diminishing then the signification of this factor can be sharply defined. The factor is in this case at least approximately equal to  $\frac{b_g - b_0}{b_1 - b_0}$ , its signification can be derived from the following equations, (comp. my paper: "The equation of state and the Theory of cyclic Motions"):

$$\left\{ M + \left( \frac{\partial P_b}{\partial b} \right)_{b=b_1} \right\} (b_1 - b_0) = RT$$

$$\left( \frac{\partial P_b}{\partial b} \right)_{b=b_g} (b_g - b_0) = RT$$

So we find for it:

$$\frac{b_g - b_0}{b_1 - b_0} = \frac{M + \left( \frac{\partial P_b}{\partial b} \right)_{b=b_1}}{\left( \frac{\partial P_b}{\partial b} \right)_{b=b_g}}.$$

The quantity  $\left( \frac{\partial P_b}{\partial b} \right)$  in this equation represents the atomic forces, which keep the molecule intact or at least contribute to the causes which keep the molecule intact. Making use of this value of  $K$  we find:

$$\log \frac{P}{M} \frac{\left(\frac{\partial P_v}{\partial b}\right)_{b=b_g}}{M + \left(\frac{\partial P_v}{\partial b}\right)_{b=b_l}} = - \frac{b_1}{RT} \dots \dots \dots (6)$$

The first member of this equation contains the logarithm of the product of two ratios, namely the ratio of the inwardly directed forces which keep the molecules — considered as separate systems — inside the vapour and the liquid phase, and the ratio of the inwardly directed forces which keep these systems in both phases intact. In the case that it is a quasi-decrease it is impossible to indicate the signification of  $K$  in such a precise manner; but the quantity  $\int_{v-b}^{db}$  differing also in this case from zero, the above considerations show with certainty that the quantity  $K$  exists also in this case. The question whether it will be larger or smaller can only be decided by a comparison of the course of  $b$  with  $v$  in the supposition of a quasi decrease with that in the supposition of a real diminishing.

The term  $\frac{1}{2} \frac{b-b_0}{v-b}$  has been neglected in equation (6). This equation applies only for low temperatures, and for those temperatures the term in question is equal to  $\frac{1}{2}$  according to the formula given for  $b$ . It is remarkable that also many other suppositions concerning the nature of the forces which keep the molecules intact, different from those suppositions which have led to the form chosen for  $b$ , yield the same equation (6), every time however only after neglection of a relatively small quantity in whose kinetic interpretation I have not yet succeeded. We obtain equation (6) when we assume, 1<sup>st</sup> that the molecule may be regarded to be a binary system consisting of two atoms or of two closely connected groups of atoms, which we shall call radicals, 2<sup>nd</sup> that these parts move relatively to each other, and 3<sup>rd</sup> that the amplitudes of these motions are of the same order as the dimensions of the atoms. If the parts are radicals, other motions take place inside those radicals, but the amplitudes of these motions are so small that they have no noticeable effect on the volume of the radicals. We have represented the forces which the atoms or radicals exercise on one another by  $a(b-b_0)$ , so in the gaseous state by  $a(b_g-b_0)$ . So, as we have derived the equation:

$$a(b_g-b_0)^2 = RT$$

and as  $b_g-b_0$  is constant,  $a$  must be proportional with the temperature, — and I must acknowledge that it is difficult to image a mechanism

for the molecule in which the forces between the two parts of which it is thought to consist, satisfy the conditions, that they are proportional with the distance, and at the same time increase proportionally with  $T$ . Perhaps we get a more comprehensive conception of a molecule, if we ascribe the forces which keep the atoms together in the molecule not to a mutual attraction of the atoms, but to the action of the general medium by which the atoms are surrounded. The molecules of a gas are free to move inside the space in which they are included and they are kept inside that space only by the action of the walls; in the same way it might be that the atoms of a molecule were free to move inside a certain space — the volume of the molecule — and that they are only prevented from separating by an enclosure of ether. Still assuming that  $b_g - b_0$  has for all temperatures the same value, we should be again obliged to conclude that the forces which keep the molecule intact are proportional with the temperature, but this conclusion would now be much less incomprehensible. According to these suppositions it is also rational to assume that the force required to split up the molecule into two atoms is the same for all temperatures. So we should obtain the formula:

$$\frac{b - b_0}{v - b} = 1 - \frac{b - b_0}{b_g - b_0}$$

With this equation we have:

$$\int_b^{b_g} \frac{db}{v - b} = \int_b^{b_g} db \left\{ \frac{1}{b - b_0} - \frac{1}{b_g - b_0} \right\} = \log \frac{b_g - b_0}{b - b_0} - \frac{b - b_0}{v - b}$$

The term which must be subtracted from  $\log \frac{b_g - b_0}{b - b_0}$  has now twice the value it had before, but the chief term has remained unchanged. In my further investigation, however, I will continue with the discussion of equation (4), because my chief aim is only to investigate the principle consequences of the nearly certainly existing diminution of  $b$ , independent of the question whether this diminution is real or only fictitious; and in doing so I will confine myself to a certain conception of the molecule — that which leads to equation (4) — as an instance.

B. *The coefficient of dilatation and the coefficient of compressibility of liquids.*

Let us again assume the temperature to be so low that  $\rho$  may be neglected compared with  $\frac{a}{v^2}$  and that we therefore have:

$$\frac{a}{v^2} (v-b) = RT.$$

The value for  $\frac{1}{v} \left( \frac{dv}{dT} \right)_p$  which we may calculate from this equation applies only to the pressure  $p = 0$ , and is therefore not the same as would be found for another constant pressure; neither is it that which corresponds to the points of the border curve. For very low temperatures the difference will probably be small. For higher temperatures the differences might be considerable; and for the temperature which is so high that the isothermal in its lowest point touches the  $v$ -axis, in which case  $\frac{1}{v} \left( \frac{dv}{dT} \right)_p = \infty$ , it would even be absurd to suppose the two values to be mutually equal.

An accurate calculation of the value of  $\frac{1}{v} \left( \frac{dv}{dT} \right)_{p=0}$  yields according to the relations chosen above:

$$\frac{T \left( \frac{dv}{dT} \right)_{p=0}}{v} = \frac{(n-1)z \left\{ 1 + \frac{1}{1-z^2} + \frac{2z^2}{(1-z^2)^2} \right\}}{1-(n-1) \left[ z + \frac{z}{1-z^2} \right] - 4(n-1)z \frac{z^2}{(1-z^2)^2}}$$

We will put  $n = 1$  and the following approximated relation:

$$\frac{T \left( \frac{dv}{dT} \right)_{p=0}}{v} = \frac{2z}{1-2z}.$$

With  $z = \frac{1}{7}$  (see p. 140) this yields 0,4 for the value of  $T\alpha_v$  or  $\alpha_v = \frac{0,4}{273}$  (for ether) = 0,00146. Our assumptions therefore appear to lead to a value for the coefficient of dilatation which does not deviate much from the experimental value.

If we had taken the form  $a e^{1 - \frac{T}{T_k}}$  for  $a$ , then the corresponding value of  $z$  would have been  $\frac{1}{13,5}$  and we should have had:

$$\frac{T \left( \frac{dv}{dT} \right)_p}{v} = \left( 1 + \frac{T}{T_k} \right) \frac{2z}{1-2z},$$

which is only about  $\frac{3}{11}$  of the true value. From this we conclude that the assumption that our relations are satisfied and that at the

same time  $a$  has the form  $a e^{-\frac{T}{T_k}}$  leads to inaccurate results.

We might also write a value for  $\left(-\frac{v dp}{dv}\right)$  or  $\frac{1}{\beta}$ , but we will calculate the coefficient only indirectly from:

$$\frac{T}{v} \left(\frac{dv}{dT}\right)_p \left(-v \frac{dp}{dv}\right) = \frac{a}{v^2}$$

or

$$0,413 \times 6000 = 27 p_k \left(\frac{b_g}{v}\right)^2$$

or with approximation:

$$1,6 = \frac{z}{1+2z},$$

which agrees with  $z = \frac{1}{8}$ .

The value of  $\beta$  calculated according to our relations may therefore be considered to be at any rate approximately accurate.

Yet it remains strange that for the liquid volume itself a calculation according to our suppositions yields a value which is much too small.

According to a table in Cont. I 2<sup>nd</sup> p. 172 the liquid volume for temperatures which do not differ much from  $\frac{1}{2} T_k$  is equal to  $0,8 b_0$ . Even if we take into account that  $b_0 < b_g$  we cannot diminish the factor  $0,8$  to less than  $0,7$ .

We have then the equation

$$0,7 b_g = b_0 (1 + 2z)$$

or

$$0,7 n = 1 + 2z.$$

With  $n = 2$ , this yields  $z = \frac{1}{5}$ , which does not agree with the value  $\frac{1}{7}$ , which we must assume for  $z$ , as we saw above. I have not yet been able to investigate, what modification must be made in the relation assumed for  $b$ ; e. g. to put  $n = 1,8$  or to suppose  $b_0$  really to be smaller at low temperatures. If we suppose  $b_0$  to be a function of the temperature, then the calculations become very intricate and difficulties of another kind arise. Therefore I prefer to regard the above considerations as conducing to point out that everything shows that  $b$  must really increase with  $v$ .

Let us investigate what consequences of general nature follow from this variability of  $b$ . In the first place we observe that the three real values of  $v$  for given temperature and given pressure cannot be calculated any more by means of an equation of the third degree. The equation of state namely may assume a very intricate form if

we substitute in it the expression for  $b$  which we get by solving the equation which expresses the variability of  $b$  with  $v$  and  $T$  — the possibility of a dependency of  $b$  on  $T$  being admitted. We shall represent the solution of this equation by

$$b = g(v, T).$$

But the general course has remained the same; e.g. the fact that for temperatures below the critical temperature a maximum and a minimum pressure occurs. The critical temperature is that for which this maximum and this minimum pressure coincide and the critical point may again be calculated from the three equations:

$$p = F(v, T),$$

$$\left(\frac{dp}{dv}\right)_T = 0$$

and

$$\left(\frac{d^2p}{dv^2}\right)_T = 0$$

If therefore we could exclude all disturbing influences, if we could neglect phenomena of capillarity and adsorption, if we could neutralize gravity, if we could keep the temperature absolutely constant throughout the space occupied by the substance, if we could perform the experiments with perfectly pure substances without the slightest trace of admixtures and if we could suppose that the equilibrium is established instantaneously, then we should have coexistence of two homogeneous phases of well defined properties for all temperatures below the critical one, and exactly at the critical temperature only one homogeneous phase of well defined properties would exist.

But the requirements enumerated here can never be fulfilled. Already below the critical temperature deviations occur. The straight line representing the evaporation parallel with the  $v$ -axis has probably never been realised as yet in connection with the circumstance that nobody has as yet experimented with a perfectly pure substance. The boiling point always varies when the distillation is continued, chiefly if we observe near the critical temperature. If in a closed vessel we heat a substance which is separated into a liquid and a vapour phase, then the properties of the liquid phase may be varied by shaking the vessel (EVERSHEIM. Phys. Zeitschr. 15<sup>th</sup> June 1903), probably in connection with the circumstance that the liquid expanding during the heating is internally cooled in consequence of the expansion and the evaporation and reaches the surrounding temperature only very slowly by conduction; and also in connection with the always occurring impurities. If further the substance is subjected to gravity, then neither vapour phase nor liquid phase is homogeneous. To

every horizontal layer corresponds another density according to the formula of hydrostatics:

$$dp = - \rho g dh.$$

For temperatures far below the critical one this circumstance is of little importance; for the critical temperature itself, however, the influence of gravity is considerable. If we write namely the formula of hydrostatics in the following form:

$$\frac{1}{\rho} \frac{dp}{d\rho} = - g \frac{dh}{d\rho}.$$

then we see that  $\frac{dp}{d\rho} = 0$  or  $\frac{dh}{d\rho} = \infty$  at that point of the height of the

vessel where the critical phase really occurs, i. e. where  $\frac{d\rho}{dh} = 0$ .

If therefore we construct a graphical representation of the successive densities, laying out the height as abscissa and the density as the ordinate, then we get a continually descending curve. In the beginning its concave side is turned downwards; at a certain point the tangent is vertical and the curve has a point of inflexion; farther the convex side is turned downwards. In the neighbourhood of the critical phase we find therefore a rapid change in the density.

The equation of state can only account for the *state of equilibrium* described above as it deals only with states of equilibrium. Another question is how that equilibrium is established and whether it is established in a longer or shorter time according to the method of investigation.

It has been observed several times in these latter years that the state of equilibrium of a quantity of a substance which is contained in a closed vessel slowly heated to the critical temperature, requires so long a time before it has been reached that some investigators have concluded that the liquid consists of other molecules than the vapour. DE HEEN, GALITZINE, TRAUBE and others speak therefore of "molecules liquidogènes" and "molecules gasogènes". Some of them suppose the "molécules liquidogènes" to be more complex, others suppose them to be only smaller. This latter supposition agrees with the ideas I have expressed in my "The equation of state and the theory of cyclic motions." And for an explanation of the fact that the equilibrium is so slowly established, these investigators refer to the slow diffusion of the heterogeneous molecules.

To this fact they refer however wrongly. The kinetic theory accounts satisfactorily for the slowness of the diffusion and has even enabled us to calculate the coefficient of diffusion for mixtures of

heterogeneous molecules which cannot pass into one another. Here however we are dealing with molecules which can pass into each other. And if in such a case the establishing of the equilibrium requires a long time, then we must account for the fact that in this case more-atomic molecules only slowly conform their size to the varied circumstances, though in other cases they can bring their internal motions so quickly into harmony with, for instance, a variation of the temperature.

I therefore think it not to be proved, that the increase of  $b$  being either a real or a quasi increase, requires a noticeable time to be brought about, till the real constancy of the temperature throughout the closed vessel and the perfect purity of the substance has been proved, which as yet is not the case.

It must be granted that the summit of the boundary curve is broadened and flattened by the variability of  $b$  and that the critical isothermal may be estimated to have a larger part which is nearly parallel with the  $v$ -axis. And this causes considerable differences of density to follow from small differences of pressure. But if no causes even for small differences of pressure can be pointed out, then the occurrence of differences of density larger than those that follow from the action of gravity cannot even be called *phenomena of retardation*, these latter being also a kind of phenomena of equilibrium.

Another observation of general nature before I conclude at least for the present these considerations on the influence of the variability of  $b$ . This variability accounts for the possibility of deviations from the law of corresponding states. If the way in which  $b$  varies with the volume is different for different substances i.e. in consequence of a different ratio of  $b_g$  and  $b_o$ , then the general course remains the same, but the isothermals become different in details. I have even begun to doubt whether the behaviour of substances containing the radical OH in the molecule — acids, alcohols, water etc., which in gaseous state present no association to double molecules and which are often indicated by the name of abnormal substances — which behaviour deviates so markedly from that of other substances, must really be ascribed to association of the molecules in the liquid state.

In connection with equation (6) (see p. 143) the question arises: Is the quantity which I have denoted by  $\frac{\partial T_b}{\partial b}$  for these substances perhaps small? Is the easy substitution of one of the components perhaps an indication of a feeble connection of the parts of the compound which involves a strong variability of the size of the molecule. The so called

abnormal substances would then be those whose molecules can undergo large variations in size. More suchlike questions arise — but I will no further discuss them without a closer investigation.

#### POSTSCRIPTUM.

When the above paper was printed I received a kind letter from Dr. GUSTAV TEICHNER, who informs me that he has sent me one of his tubes filled with  $\text{CCl}_4$  in which he has succeeded in strikingly showing the large differences in density at the critical temperature by means of floating glass spheres whose specific gravity has been determined accurately. He himself however acknowledges emphatically: “dass diese Erscheinungen insofern keine Gleichgewichtszustände vorstellen, als die Phasen in Berührung mit einander sich äusserst langsam (beim Rühren sofort) zu einer homogenen Mischung vereinigen.”

The equation of state deals only with states of equilibrium as I have observed already before. Discussing these anomalies as I have done in this paper, I treated questions which properly speaking lie outside my subject. I have mentioned them, because I also expected for a moment that the variability of  $b$  assumed by me, might account for the slowly establishing of the state of equilibrium. But this is only the case if we assume, that the molecule does not immediately assume the size which agrees with the value of  $T$  and  $v$  — and this seems after all to be improbable to me, though I acknowledge that molecular transformations occur which proceed slowly. The expectation of Dr. TEICHNER, that the theory would lead to two really homogeneous phases is inaccurate in consequence of the action of gravity — as has been shown already before i. a. by GOUY. Not the phenomenon itself as it is seen, is anomalous, only the differences of the density are anomalously large. It is true that Dr. TEICHNER writes to me that he has ascertained that the temperature was constant but even a difference of temperature of  $\frac{1}{100}$  degree yields a very considerable difference in density. For densities which are larger than the critical one we have:

$$\frac{T}{p} \frac{dp}{dT} > \xi$$

$\xi \frac{p}{T}$  being comparable to unity. If therefore in a point the temperature is  $\frac{1}{100}$  degree too low, a diminishing of the pressure with

an amount of about  $\frac{1}{100}$  atmosphere will keep such a phase in equilibrium, at least as far as the pressure is concerned. And a cause which accounts for a difference of pressure of about  $\frac{1}{100}$  atmosphere accounts also for considerable differences in density as the critical isothermal runs nearly horizontally in the neighbourhood of the critical point.

A return to the time when we thought to explain a thing by speaking of solubility and insolubility, seems not to be desirable to me.

**Chemistry.** — “*On the possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances.*” By J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

I. The occurrence of so called “*eutectic points*” in *meltingpoint-curves* does not seem to agree with the supposition of *perfect isomorphy* of the two solid components and of their mixtures. This fact has been repeatedly pointed out. It has been assumed that an interruption in the curve representing the solid mixtures (as in fig. 1 of the plate) can only occur for *isodimorphous* substances, and that the series of mixtures in the case of isomorphous substances was necessarily to be uninterrupted (as in fig. 2).

Lately STORTENBEKER <sup>1)</sup> expressed again the same idea and this induced me to subject the question to a closer investigation. In the following paper I hope to show that an interruption in the series of the mixtures can very well occur even for *perfectly isomorphous* substances. In order to do this we must keep in view that — especially in the *solid* condition — *unstable* phases may occur, and that in all occurring cases it is possible to trace the meltingpoint-curve *continuously through the eutectic point*. Only the stable conditions which generally lie above the eutectic point are liable to be realized, so the series of the mixtures is interrupted only *practically*.

Prof. BAKHUIS ROOZEBOOM has expressed the idea of prolonging the meltingpoint-curve beyond the eutectic point already before; the way however in which we must think this to be performed is indicated inaccurately in the figure of an earlier paper of STORTENBEKER <sup>2)</sup>.

<sup>1)</sup> Ueber Lücken in der Mischungsreihe bei isomorphen Substanzen, Zeitschrift für Ph. Ch. **43**, 629 (1903).

<sup>2)</sup> Ueber die Löslichkeit von hydratierten Mischkrystallen, Z. f. Ph. Ch. **17**, 645 (1895).

The following considerations are an abbreviated survey of a more elaborate paper which will be published elsewhere <sup>1)</sup>.

II. I have shown in a previous communication <sup>2)</sup>, that we may express the *molecular* thermodynamic potentials of the two components of a *liquid* mixture — if we assume the equation of state of VAN DER WAALS — as follows:

$$\left. \begin{aligned} \mu_1 &= e_1 - c_1 T - (k_1 + R) T \log T + \frac{a_1 x^2}{(1+rx)^2} + RT \log(1-x) \\ \mu_2 &= e_2 - c_2 T - (k_2 + R) T \log T + \frac{a_2(1-x)^2}{(1+rx)^2} + RT \log x \end{aligned} \right\} .$$

The different quantities occurring in these equations have the well known signification, indicated in the paper quoted above.

In order to simplify the calculation we shall always assume in the following, that  $r \left( = \frac{-b_1 + b_2}{b_1} \right) = 0$ , and therefore that the equations  $a_1 = \frac{A}{b_1^2}$  and  $a_2 = \frac{A}{b_2 b_1^2}$  are identically satisfied,  $A$  representing  $a_1 b_2^2 - 2 a_{12} b_1 b_2 + a_2 b_1^2$ . This assumption comes to the same as the supposition that the molecular volumes of the two components differ only slightly, which supposition may be considered to be justified, as the terms  $\frac{a_1 x^2}{(1+rx)^2}$  and  $\frac{a_2(1-x)^2}{(1+rx)^2}$  represent the mutual influence of the two components in the mixture only *approximately*.

In the second place I shall assume that the above expressions also apply to the *solid* state, an assumption which we may expect to be satisfied in first approximation, as the case we are dealing with, namely that of *mixed crystals* or *solid solutions* <sup>3)</sup>, shows in many respects the greatest analogy with liquid solutions.

If we also suppose  $r$  in the solid phase to differ little from zero, and if we indicate all quantities in that phase with accents, then we may write:

For the *liquid* phase:

$$\left. \begin{aligned} \mu_1 &= e_1 - c_1 T - (k_1 + R) T \log T + a x^2 + RT \log(1-x) \\ \mu_2 &= e_2 - c_2 T - (k_2 + R) T \log T + a(1-x)^2 + RT \log x \end{aligned} \right\} .$$

For the *solid* phase:

$$\left. \begin{aligned} \mu'_1 &= e'_1 - c'_1 T - (k_1 + R) T \log T + a' x'^2 + RT \log(1-x') \\ \mu'_2 &= e'_2 - c'_2 T - (k_2 + R) T \log T + a'(1-x')^2 + RT \log x' \end{aligned} \right\} . \quad (1)$$

<sup>1)</sup> In the *Archives Teyler*.

<sup>2)</sup> These proceedings April 24, 1903.

<sup>3)</sup> Mixed crystal will always be treated here as *solid solutions*, though in these latter years difficulties have sometimes arisen against this view. See i.a. STORTENBEKER, l.c., p. 633.

The components are in equilibrium in both phases if

$$\mu_1 = \mu'_1 \quad ; \quad \mu_2 = \mu'_2,$$

so that we get (the terms with  $T \log T$  cancel each other):

$$\left. \begin{aligned} e_1 - c_1 T + \alpha x^2 + RT \log (1-x) &= e'_1 - c'_1 T + \alpha' x'^2 + RT \log (1-x') \\ e_2 - c_2 T + \alpha (1-x)^2 + RT \log x &= e'_2 - c'_2 T + \alpha' (1-x')^2 + RT \log x' \end{aligned} \right\}$$

or with

$$e_1 - e'_1 = q_1 \quad , \quad e_2 - e'_2 = q_2 \quad , \quad c_1 - c'_1 = \gamma_1 \quad , \quad c_2 - c'_2 = \gamma_2 :$$

$$RT \log \frac{1-x'}{1-x} = q_1 - \gamma_1 T + (\alpha x^2 - \alpha' x'^2)$$

$$RT \log \frac{x'}{x} = q_2 - \gamma_2 T + [\alpha(1-x)^2 - \alpha'(1-x')^2]$$

If we pay attention to the circumstance that for  $x=0$ ,  $x'=0$  the quantity  $T$  must be equal to  $T'_1$ , and in the same way  $T=T'_2$  for  $x=1$ ,  $x'=1$  ( $T'_1$  and  $T'_2$  are the meltingtemperatures of the pure components), then we may write:

$$\gamma_1 = \frac{q_1}{T'_1} \quad , \quad \gamma_2 = \frac{q_2}{T'_2} .$$

We have therefore

$$T \left( \frac{q_1}{T'_1} + R \log \frac{1-x'}{1-x} \right) = q_1 + (\alpha x^2 - \alpha' x'^2)$$

$$T \left( \frac{q_2}{T'_2} + R \log \frac{x'}{x} \right) = q_2 + [\alpha(1-x)^2 - \alpha'(1-x')^2]$$

or with

$$\alpha = q_1 \beta \quad , \quad \alpha' = q_1 \beta' :$$

$$T = T_1 \frac{1 + (\beta x^2 - \beta' x'^2)}{1 + \frac{RT_1}{q_1} \log \frac{1-x'}{1-x}} = T_2 \frac{1 + \frac{q_1}{q_2} [\beta(1-x)^2 - \beta'(1-x')^2]}{1 + \frac{RT_2}{q_2} \log \frac{x'}{x}} \dots (2)$$

These are the two fundamental equations from which we may calculate the values of  $x'$  and  $T$  corresponding to each given value of  $x$ , and which represent a course of the meltingpoint-curve which is perfectly continuous, at least theoretically.

It is easy to see that in the case that no mixed crystals occur,  $x'$  is continuously equal to zero, and the equation is reduced to

$$T = T_1 \frac{1 + \beta x^2}{1 - \frac{RT_1}{q_1} \log (1-x)},$$

an equation which I have already deduced in a previous paper. But in the present paper we will assume that the mixing-proportion

in which one of the components occurs in the solid phase, though in the extreme case it can be exceedingly small (i. e. practically equal to zero), yet in general can never be rigorously equal to zero. In this way the *continuity* remains preserved, and we may give all possible values to the quantities  $\beta$  and  $\beta'$  — as to  $\beta'$  from 0 to  $\infty$ .

We shall observe here at once that the quantity which dominates the whole phenomenon is the quantity  $\beta'$  of the *solid* phase. When this quantity has a high value, the solid phase will contain only a very small trace of one of the two components, and only when the value of this quantity becomes comparable with the corresponding quantity  $\beta$  in the liquid phase, the case of fig. 2 can occur. It is therefore of the highest importance to know the exact signification of these quantities  $\beta$  and  $\beta'$ , or rather of the quantities  $\alpha = q_1 \beta$  and  $\alpha' = q_1 \beta'$ .

From the above deductions appears namely that the quantity  $\alpha x^2$  does not represent anything else but the absorbed *latent heat* required for the *mixing* per Gr. Mol. for the case that an infinitely small quantity of one of the components is mixed with the solution in which the mixing-proportion for this component is  $1 - x$ . In the same way the quantity  $\alpha(1-x)^2$  represents the latent heat for the other component in this solution. The quantity  $\alpha$  itself is therefore the latent heat for the first component for  $x = 1$ ; i. e. for the case that the first component is mixed with a solution which consists exclusively of the second component — or we may also say that  $\alpha$  is the latent heat for the second component for  $x = 0$ ; i. e. for the case that this component is mixed with a solution consisting exclusively of the first. The fact that these two quantities of latent heat are the same is a consequence of our supposition  $b_1 = b_2$ , from which follows that  $\alpha_1 = \frac{1}{b_1^3}$  is equal to  $\alpha_2 = \frac{1}{b_2 b_1^2}$ . In reality these two quantities will not always be equal.

That the signification we have ascribed to the quantities  $\alpha x^2$  and  $\alpha(1-x)^2$  is the true one, may be shown from the numerators of equation (2), which being respectively multiplied with  $q_1$  and  $q_2$ , represent the *total* latent heats of liquefaction  $w_1$  and  $w_2$ , namely

$$\left. \begin{aligned} w_1 &= q_1 (1 + \beta x^2 - \beta' x'^2) = q_1 + \alpha x^2 - \alpha' x'^2 \\ w_2 &= q_2 \left( 1 + \frac{q_1}{q_2} [\beta (1-x)^2 - \beta' (1-x')^2] \right) = q_2 + \alpha (1-x)^2 - \alpha' (1-x')^2 \end{aligned} \right\} \cdot (3)$$

The total latent heat required for the liquefaction is therefore equal to the *pure* latent heat of liquefaction, *augmented* with the latent heat required for the mixing of the liquid phase, *diminished* with that required for the mixing of the solid phase.

A high value for  $\alpha$  (or  $\beta$ ) means therefore a high value of the latent heat of mixing, and when we shall presently see that a high value of  $\beta'$  leads to very small values of  $x'$  or of  $1-x'$ , this circumstance may be interpreted as follows:

If a large amount of energy is required in order to make one of the solid components enter into the solid solution (or the mixed crystal) then this solid solution will contain only a slight trace of one of these two components.

III. We now proceed to the discussion of the fundamental equations (2).

Let us in the first place determine the quantities  $\frac{dT}{dx}$  and  $\frac{dT}{dx'}$  by *totally* differentiating the conditions of equilibrium —  $\mu'_1 + \mu_1 = 0$  and —  $\mu'_2 + \mu_2 = 0$  according to  $T$ . After several transformations we get:

$$\frac{dT}{dx} = -T \frac{(x-x') \frac{\partial^2 \zeta}{\partial x^2}}{(1-x')w_1 + x'w_2} ; \quad \frac{dT}{dx'} = -T \frac{(x-x') \frac{\partial^2 \zeta'}{\partial x'^2}}{(1-x)w_1 + xw_2} \quad . \quad . \quad (4)$$

These well known equations have been deduced several times<sup>1)</sup>, i. a. by Prof. VAN DER WAALS for the analogous equilibrium of liquid and gaseous phases.

From (4) we may deduce the quantity  $\left(\frac{dT}{dx}\right)_0$ , i. e. the *initial direction* of the meltingpoint-curve.

As  $\frac{\partial \mu_1}{\partial x} = -\frac{RT}{1-x} + 2\alpha x$ , we have

$$\frac{\partial^2 \zeta}{\partial x^2} = -\frac{1}{x} \frac{\partial \mu_1}{\partial x} = \frac{RT}{x(1-x)} - 2\alpha,$$

therefore, for  $x = 0$ ,  $T = T_1$

we have:  $\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_0 = \frac{RT_1}{x_0}$ ,

if we write  $x_0$  for  $x = 0$ . For  $x = 0$  we have also  $x' = 0$ . The denominator of  $\frac{dT}{dx}$  appears therefore to be equal to  $(w_1)_0 = q_1$ , hence

$$\left(\frac{dT}{dx}\right)_0 = -T_1 \frac{(x_0 - x'_0) \frac{RT_1}{x_0}}{q_1} = -\frac{RT_1^2}{q_1} \left(1 - \frac{x'_0}{x_0}\right),$$

<sup>1)</sup> See i. a. my Lehrbuch der math. Chemie, p. 118 and 123—124. (Leipzig, J. A. BARTH, 1901).

from which follows that —  $q_1$  being supposed to be *positive* — the value of  $\left(\frac{dT}{dx}\right)_0$  can only be positive if  $\frac{x_0'}{x_0}$  should be greater than unity. Let us therefore determine the limiting value of  $\frac{x_0'}{x_0}$ . With  $T = T_1$ ,  $x = 0$ ,  $x' = 0$  we may derive from the equations (2):

$$T = T_2 \frac{1 + \frac{q_1}{q_2}(\beta - \beta')}{1 + \frac{RT_2}{q_2} \log \frac{x_0'}{x_0}}$$

and we have:

$$\log \frac{x_0'}{x_0} = \frac{q_2}{R} \left( \frac{1 + \frac{q_1}{q_2}(\beta - \beta')}{T_1} - \frac{1}{T_2} \right).$$

Therefore the value of  $\frac{x_0'}{x_0}$  remains smaller than unity, and the meltingpoint-curve continues to *descend*, as long as we have:

$$\beta - \beta' < \frac{q_2}{q_1} \left( \frac{T_1}{T_2} - 1 \right) \dots \dots \dots (5)$$

In the following we will always assume  $T_1 > T_2$  or  $\frac{T_1}{T_2} - 1$  positive. The above condition will then the sooner be satisfied, according as  $\beta'$  in the solid phase has a *higher positive* value. Now probably  $\beta$  will nearly always have a very small positive value and  $\beta'$  a rather large positive value. The condition will therefore probably be nearly always satisfied. If we put  $\beta = 0$ , then we get simply:

$$-a' = -q_1 \beta' < q_2 \left( \frac{T_1}{T_2} - 1 \right).$$

If  $\beta'$  (or  $a'$ ) is *positive*, i. e. if heat is *absorbed* in mixing the *solid* phase, then we shall *always* have  $\frac{x_0'}{x_0} < 1$  and therefore the meltingpoint curve will *always descend* on the side of the *highest* temperature. An initially ascending part and in connection with this the occurrence of a maximum-meltingtemperature is therefore *almost totally excluded*. The *possibility* of a maximum exists only in the *exceptional and nearly inconceivable* case, that  $\beta'$  has a much smaller positive value than  $\beta$ , or even a negative value.

If we determine  $\left(\frac{dT}{dx}\right)_{x=1}$  at the side of the *lowest* temperature quite in the same way, then we find, denoting  $1 - x$  by  $y$ :

$$\left(\frac{dT}{dx}\right)_{x=1} = -\frac{RT_2^2}{q_2} \left(1 - \frac{y_0'}{y_0}\right).$$

where:

$$\log \frac{y_0'}{y_0} = \frac{q_1}{R} \left( \frac{1 + (\beta - \beta')}{T_2} - \frac{1}{T_1} \right).$$

The quantity  $\frac{y_0'}{y_0}$  is therefore always smaller than unity if

$$\beta - \beta' < \frac{T_2}{T_1} - 1. \quad \dots \quad (5bis)$$

The second member being negative, this condition can only be satisfied if  $\beta'$  has a *high positive* value. Two cases may therefore occur, according to  $\beta'$  being larger or smaller. In the first case the initial part of the curve near  $T_2$  descends again and a *minimum* will therefore occur (fig. 2). In the second case the curve ascends near  $T_2$ ; it will therefore descend continuously from  $T_1$  to  $T_2$  without presenting a minimum.

For the case  $T_1 = T_2$  the conditions (5) and (5<sup>a</sup>) pass into

$$\beta - \beta' < 0,$$

and a *minimum* will always in this case occur if  $\beta' > \beta$ , and probably this will always be the case.

The same considerations apply of course for  $\left(\frac{dT}{dx'}\right)_0$ .

In the above considerations we have tacitly assumed that *anomalous* components occur in neither of the phases; formation of *complex* molecules or *dissociation* are therefore always excluded in the cases which we consider. When one or both of the components of the solid phase for instance consist totally or partially of double molecules, then the occurrence of a *maximum* is not excluded at all.

We now proceed to the discussion of the equations (2) for different values of  $\beta'$ , starting with very high values.

IV. In the following we shall always put  $\beta = 0$  (in the liquid phase). This simplifies the calculations in a high degree and it does not alter the results qualitatively. The equations (2) then take the following form:

$$T = \frac{T_1 (1 - \beta' x'^2)}{1 + \frac{RT_1}{q_1} \log \frac{1-x'}{1-x}} = \frac{T_2 \left(1 - \frac{q_1}{q_2} \beta' (1-x')^2\right)}{1 + \frac{RT_2}{q_2} \log \frac{x'}{x}}. \quad \dots \quad (6)$$

Let us further assume the following values, in order to be able to execute the calculations *numerically*:

$$\begin{array}{l|l} T_1 = 1200 & q_1 = 2400 \text{ Gr. cal.,} \\ T_2 = 500 & q_2 = 2000 \quad \text{''} \end{array}$$

Then we get ( $R = 2$ ):

$$T = \frac{1200(1-\beta'x'^2)}{1 + \log \frac{1-x'}{1-x}} = \frac{500(1-1,2\beta'(1-x')^2)}{1 + \frac{1}{2} \log \frac{x'}{x}} \dots \dots (6^a)$$

We will begin with assuming  $\beta'$  to be very large, e. g.  $\beta' = 5$ . As we have  $a' = q_1 \beta'$  this means that the latent heat of mixing for the first component when  $x=1$  (or of the second when  $x=0$ ) is five times as great as the latent heat of solidification of the first component. From the above equation:

$$T = \frac{1200(1-5x'^2)}{1 + \log \frac{1-x'}{1-x}} = \frac{500(1-6(1-x')^2)}{1 + \frac{1}{2} \log \frac{x'}{x}}$$

we may calculate the temperature  $T$  corresponding to an arbitrarily chosen value of  $x$ , the value of  $x'$  being exceedingly small. So we get for  $T$ :

$$T = \frac{1200}{1 - \log(1-x)}$$

and for  $x'$ :

$$1 + \frac{1}{2} \log \frac{x'}{x} = -\frac{25}{12} (1 - \log(1-x)).$$

The following table I (p. 159) gives a survey of the corresponding values of  $x$ ,  $x'$  and  $T$ .

This represents the branch  $AA'$  of the meltingpoint-curves which starts from  $1200^\circ$  (see fig. 3).  $AB'$  is the curve  $T = f(x')$ .

If we put  $1-x = y$  and  $1-x' = y'$  then we have the equations

$$T = \frac{500(1-6y'^2)}{1 + \frac{1}{2} \log \frac{1-y'}{1-y}} = \frac{1200(1-5(1-y')^2)}{1 + \log \frac{y'}{y}}$$

from which we may calculate a new series of corresponding values of  $x$ ,  $x'$  and  $T$ . So we get the branch  $BB'$  starting from  $500^\circ$  ( $BA'$  is again the curve  $T = f(x')$ ). The value of  $y'$  being in this case very small,  $T$  may again be calculated from

$$T = \frac{500}{1 - 0,5 \log(1-y)}$$

and  $y'$  from

TABLE I.

$x$	$T$	$\frac{x'}{x} \times 10^4$	$x' \times 10^5$
0	1200	21	0
0.1	1086	14	14
0.2	981	8.3	17
0.3	884	4.8	14
0.4	794	2.6	10
0.5	709	1.2	6
0.6	626	0.46	3
0.7	545	0.14	1
0.8	460	0.026	0.2
0.9	363	0.0014	0.01
0.95	300	0,...	0,...
0.97	266	0,...	0,...
0.99	214	0,...	0,...
1	0	0	0

TABLE II.

$y$	$T$	$\frac{y'}{y} \times 10^5$	$y' \times 10^7$
0	300	25	0
0.1	475	15	15
0.2	450	8.6	17
0.3	424	4.5	14
0.4	398	2.0	8
0.5	371	0.89	4
0.6	343	0.31	2
0.7	312	0.078	0.5
0.8	277	0.11	0.09
0.9	232	0.00040	0.006
0.95	200	0,...	0,...
0.97	185	0,...	0,...
0.99	151	0,...	0,...
1	0	0	0

$$1 + \log \frac{y'}{y} = -\frac{48}{5} (1 - 0,5 \log (1 - y)).$$

The values calculated in this way are found in table II (see above).

The values found for  $y'$  are even smaller than those for the first branch. In both branches we clearly see the occurrence of a *maximum* in the curves  $T = f(x')$ , from which point the value  $x'$  (or  $y'$ ) does not increase any more, but falls again to zero.

The position of that maximum may be easily found from the general equation (4) for  $\frac{dT}{dx}$ . The tangent running vertically, the denominator  $(1-x)w_1 + xw_2 = 0$  must be zero and therefore we have, as we have assumed  $\beta$  to be equal to zero:

$$(1-x)q_1(1-\beta'^2x^2) + xq_2(1-\frac{q_1}{q_2}\beta'(1-x)^2) = 0.$$

Neglecting  $x'$  we get :

$$(1-x)q_1 + xq_2 \left(1 - \frac{q_1}{q_2}\beta'\right) = 0,$$

and therefore

$$x_m = \frac{q_1}{q_1 + q_2 \left( \frac{q_1}{q_2} \beta' - 1 \right)} = \frac{q_1}{q_1 - q_2 + q_1 \beta'} \cdot \cdot \cdot \cdot \quad (7)$$

Introducing our values for  $q_1$  and  $q_2$  and  $\beta' = 5$ , we get  $x_m = {}^6/_{31} = \underline{0,19}$ .

With this value corresponds  $T'_m = \frac{1200}{1,211} = \underline{991^\circ}$ . Further we have

$\left( \frac{x'}{x} \right) = 0,00087$ , and therefore  $x'_m = \underline{0,00017}$ , which agrees with the value found in the first table for the first branch.

For the second branch we have exactly in the same way:

$$y_m = \frac{q_2}{q_2 + q_1 (\beta' - 1)} = \frac{q_2}{q_2 - q_1 + q_1 \beta'} \cdot \cdot \cdot \cdot \quad (7bis)$$

With  $\beta' = 5$  this yields  $y_m = {}^5/_{29} = \underline{0,17}$ .

$T_m$  is there  $\frac{500}{1,093} = \underline{457^\circ}$ ,  $\left( \frac{y'}{y} \right)_m = 0,000010$ , and therefore  $y'_m = \underline{0,0000017}$ , which value again agrees with that found in the second table.

If  $x'_1$  and  $x'_2$  represent the proportions in which the second component occurs in the two solid phases which coexist in the *eutectic* point  $C$  with the liquid phase  $x$ , then the point  $C$  may be found by solving a double set of equations (6), namely those with  $x'_1$  and those with  $x'_2$ . From these equations the quantities  $T$ ,  $x$ ,  $x'_1$  and  $x'_2$  may be solved.

If  $x'_1$  and  $1 - x'_2$  may be neglected, then we get simply:

$$T = \frac{T_1}{1 - \frac{RT_1}{q_1} \log(1-x)} = \frac{T_2}{1 - \frac{RT_2}{q_2} \log x} \cdot \cdot \cdot \cdot \quad (8)$$

from which follows after introduction of our values for  $T_1$ , etc.  $x = \underline{0,809}$ ,  $T = \underline{452^\circ}$ .

The corresponding values of  $x'$  and  $y'$  ( $x'_1$  and  $1 - x'_2$ ) may be calculated as has been done above. (Compare also the tables for  $x = 0,8$ ).

A closer consideration of the equations (6) shows (comp. fig. 3), that besides the branches mentioned above a third branch exists, which may to some extent be regarded as the connecting curve of the two former ones. This branch, however, lies wholly within the region of the *negative* absolute temperatures and has therefore only mathematical importance for the continuity of the meltingpoint-curve. The curve  $T = f(x)$ , namely  $A'DB'$  forms the connection between

$AA'$  and  $BB'$ .  $EDF$  is the corresponding curve  $T = f'(x')$ , which touches  $A'DB'$  in the common minimum  $D$ , where  $x = x'$ .

The point  $D$  is therefore determined by the equations

$$T = T_1(1 - \beta'x^2) = T_2\left(1 - \frac{q_1}{q_2}\beta'(1-x)^2\right), \dots \dots (9)$$

or with our values:

$$T = 1200(1 - 5x^2) = 500(1 - 6(1-x)^2),$$

which gives  $x = x' = 0,494$ ,  $T = -264^\circ$ .

The point  $E$  indicates another value of  $x'$ , corresponding to the point  $A'$  of the curve  $T = f'(x)$ , where  $x = 1$ , but now  $T = -0^\circ$ . This point is obviously determined by the equation (comp. (6))

$$1 - \frac{q_1}{q_2}\beta'(1-x')^2 = 0 \quad (\text{therefore } w_2 = 0), \dots \dots (10)$$

which yields  $x' = 0,592$ .

The point  $F$  indicates a value of  $x'$  corresponding to the point  $B'$  of the curve  $T = f'(x)$ , where  $x = 0$ ,  $T = -0^\circ$ . Now we have:

$$1 - \beta'x'^2 = 0 \quad (\text{therefore } w_1 = 0), \dots \dots (10bis)$$

from which follows:  $x' = 0,447$ .

The curve  $T = f'(x)$  has therefore obtained a continuous course through the points  $A'$  and  $B'$ , the curve  $T = f'(x')$  however changes abruptly at  $B'$  from  $B'$  to  $E$ , and at  $A'$  from  $A'$  to  $F$ ; further its course is continuous from  $E$  through  $D$  to  $F$ .

The question might be put: in what case does the point  $E$  come in  $A'$  and the point  $F$  in  $B'$  and has the discontinuity in the curve  $T = f'(x')$  therefore reached its highest possible value? Obviously this is the case for  $\beta' = \infty$ . For then  $w_2 = 0$  can vanish for  $x' = 1$  and  $w_1$  for  $x' = 0$ . In this case the lines  $A'D$  and  $ED$  coincide over their whole length with the axis  $x = 1$ , and the lines  $B'D$  and  $FD$  with the axis  $x = 0$ .

At all temperatures above the absolute zero the values of  $x'$  and  $y'$  vanish in this case continuously; this represents therefore the case, that the solid phase contains only *one* component.

The lines  $A'DB$  and  $EDF$  lie, as we have seen, wholly in the region of negative absolute temperatures; besides this they lie with their whole course in the region of the *unstable* phases, as is shown by a closer examination of the relations

$$\frac{\partial^2 \xi}{\partial x^2} = \frac{RT}{x(1-x)}; \quad \frac{\partial^2 \xi'}{\partial x'^2} = \frac{RT}{x'(1-x')} - 2a'.$$

V. The value of  $\beta'$ , for which the point  $D$ , where  $x = x'$ , is found exactly at  $T = 0$ , may be calculated by solving the equations

$$0 = T_1(1 - \beta'x^2) = T_2\left(1 - \frac{q_1}{q_2}\beta'(1 - x'^2)\right),$$

which yield :

$$\beta' = \left(1 + \sqrt{\frac{q_2}{q_1}}\right)^2; \quad x' = \left(1 + \sqrt{\frac{q_2}{q_1}}\right)^{-1}, \quad . . . \quad (11)$$

i. e. with our values of  $q_1$  and  $q_2$ ;  $\beta' = \underline{3,659}$  and  $x' = \underline{0,523}$ .

The whole curve  $EDF$  or  $T=f(x')$  of fig. 3 has here contracted to the single point  $D$  (see fig. 4), and the curve  $A'DB'$  or  $T=f(x)$  is degenerated into a *straight* line, *all* whose values coexist with that one value of  $x'$ .

This line  $A'DB'$  and the point  $D$  still represent *unstable* phases.

If for this case we calculate the maxima for  $x'$  and  $y'$  of the two principle branches as we have done above, then we find:

$$x_m = 0,26, \quad T_m = 922^\circ, \quad x'_m = 0,00088.$$

$$y_m = 0,24, \quad T_m = 439^\circ, \quad y'_m = 0,000062.$$

The maximum value for  $x'$  appears to have increased to about 5 times the value it had with  $\beta' = 5$ , and that for  $y'$  to about 36 times its former value. The maximum value for  $y'$  now lies *below* the eutectic point. A simple calculation may show that in our case this already happens as soon as  $\beta'$  becomes smaller than 4,55. The maximum on the other side will require a much smaller value of  $\beta'$  before it descends below the eutectic point.

As soon as  $\beta'$  becomes smaller than  $\left(1 + \sqrt{\frac{q_2}{q_1}}\right)^2$  or with our assumptions  $< 3,66$ , the curve  $A'DB'$  begins to turn upwards and we get the course indicated in fig. 5 for e. g.  $\beta' = 2,5$ .

The line  $A'DB'$  lies now wholly in the *stable* region for  $T=f(x)$ ,  $\frac{\partial^2 \mathfrak{S}}{\partial x^2}$  being henceforth always positive. The line  $EDF$  on the other hand lies wholly in the *unstable* region for  $T=f(x')$ , as easily appears from the expression for  $\frac{\partial^2 \mathfrak{S}'}{\partial x'^2}$ . This latter circumstance however is not permanently fulfilled; by continually diminishing  $\beta'$ , a point of  $EDF$  may be reached for which  $\frac{\partial^2 \mathfrak{S}'}{\partial x'^2}$  is equal to zero and this is a condition for a further change of the shape of the melting-point curve. But this will be treated in another chapter.

The maximum values for  $x'$  and  $y'$  are now the following (namely for  $\beta' = 2,5$ ):

$$x_m = 0,375, \quad T_m = 816^\circ, \quad x'_m = 0,0044.$$

$$y_m = 0,357, \quad T_m = 410^\circ, \quad y'_m = 0,0016.$$

Gradually  $x'$  and  $\eta'$  assume practically measurable values.

We find from (9) for the maximum  $D$ :

$$x = x' = \underline{0,571}; \quad T = \underline{223^\circ}.$$

We find for  $E$ ,  $x' = \underline{0,423}$ ; for  $F$ ,  $x' = \underline{0,633}$  (see (10) and (10<sup>bis</sup>)).

VI. We now proceed to the description of the further development of the parts of the meltingpoint-curve lying below  $C$ .

According as  $\beta'$  decreases, the curve  $A'DB$  mounts higher and higher and finally it will touch the line  $BB'$ , e.g. in  $P$  (Comp. fig. 6). But the values of  $x$  and  $T$  of both curves  $T=f(x)$  coinciding in  $P$ , the values of  $x'$  also will necessarily coincide — or in other words the curves  $BA'$  and  $EDF$  will meet at the same time, namely

in the point  $Q$ . In this point however  $\frac{\partial^2 \zeta'}{\partial x'^2}$  must vanish, as  $P$  may be regarded as a *cuspid* in the continuous curve  $AA'DPB$ . If therefore we trace in the figure the curve  $\frac{\partial^2 \zeta'}{\partial x'^2} = 0$ , — i.e.  $T = a' x' (1-x') = \eta_1 \beta' x' (1-x')$ ,

which will be a *parabolic* curve, whose axis of symmetry is the ordinate  $x = 1/2$ , and whose summit lies lower according as  $\beta'$  decreases — then the curves  $BA'$  and  $EDF$  meet this curve at the same time in  $Q$ .

The direction of the two curves  $BA'$  and  $EDF$  will there *not* be horizontal, as appears immediately from the direction of the curve  $\frac{\partial^2 \zeta'}{\partial x'^2} = 0$  in the point  $Q$ . Therefore not only the numerators in the

expressions for  $\frac{dT}{dx'}$  of those two curves must vanish in consequence

of the factor  $\frac{\partial^2 \zeta'}{\partial x'^2}$ , but also the denominators  $(1-x)w, +xw_2$ . In other words:

the two curves will meet each other at the place of their *maxima* for  $x'$  and  $1-x'$ , exactly at a point where both curves had a vertical

tangent a moment before. So the expressions for  $\frac{dT}{dx'}$  are undetermined

in  $Q$  and the real direction of the pieces  $BQ$  and  $A'Q$ ,  $DQ$  and  $FQ$  must be determined in another way.

Fig. 7 represents the position of the different lines a moment later.  $\beta'$  is here somewhat smaller than in fig. 6. It may be clearly seen that the lower branches  $B'P'B'$  and  $A'Q'F$  have got detached; henceforth they are isolated and disappear more and more downwards according as  $\beta'$  decreases. They may be regarded as *rudiments* of the original meltingpoint-curve. The upper parts form henceforth the proper

meltingpoint-curve, namely  $AA'DPB$ , constituting the line  $T = f(x)$ , and  $AB'EDQB$ , constituting the corresponding line  $T = f(x')$ . The curves  $T = f(x')$  now run horizontally in  $Q$  and  $Q'$ , in consequence of the relation  $\frac{\partial^2 \zeta'}{\partial x'^2}$ , for the denominator  $(1-x)w_1 + xw_2$  no longer vanishes for both curves at the same time. The places in the two curves where this occurred before (we may imagine them to lie between  $Q$  and  $Q'$ ) have henceforth disappeared. These points  $Q$  and  $Q'$  of the curves  $T = f(x')$  correspond to the two cusps  $P$  and  $P'$  of the curves  $T = f(x)$ .

The process of detaching, described above, took place on the side of  $B$  — i. e. on the side of the highest temperature — but we shall see that the same process is repeated on the side of  $A$ , when  $\beta'$  still further decreases, which is represented in the figures 8 and 9.

The *second* detaching takes place at  $R$  and  $S$  and gives rise to two new rudimentary parts of the original meltingpoint curve on the lower side. The proper meltingpoint-curve is now  $ARDPB$  for  $T = f(x)$ , and  $ASDQB$  for  $T = f(x')$ . The two points  $S$  and  $S'$ , where the curves  $T = f(x')$  run horizontally in consequence of the relation  $\frac{\partial^2 \zeta'}{\partial x'^2} = 0$  correspond with the new cusps  $R$  and  $R'$  in the lines  $T = f(x)$ .

It is of course important to know at what values of  $\beta'$  the two processes of detaching described above, take place.

In the point  $Q$  (fig. 6) we have in the first place  $\frac{\partial^2 \zeta'}{\partial x'^2} = 0$  or  $T = q_1 \beta' x' (1-x')$ ; but we have there also  $(1-x)w_1 + xw_2 = 0$ , from which follows:

$$x = \frac{w_1}{w_1 - w_2} \quad ; \quad 1-x = \frac{-w_2}{w_1 - w_2} \quad . \quad . \quad . \quad (12)$$

In connection with the equations (6) and taking into account the equations (3) for  $w_1$  and  $w_2$ , we may deduce from these relations a set of transcendental equations from which the quantities  $T$ ,  $x'$  and  $\beta'$  may be solved by successive approximations. So we find for the *first* detaching with the values assumed by us for  $T_1$  etc.:

$$\beta' = \underline{1.545} \quad , \quad x' = \underline{0.9108(Q)} \quad , \quad x = \underline{0.2555(P)} \quad , \quad T = \underline{301.2}.$$

For the *second* we find as second solution:

$$\beta' = \underline{1.1020} \quad , \quad x' = \underline{0.1149(S)} \quad , \quad x = \underline{0.9705(R)} \quad , \quad T = \underline{268^{\circ}.9}.$$

The case of fig. 9, i. e. *just after the second detaching*, has been calculated by me point for point throughout its course, putting  $\beta'$

equal to 1.1. The following tables represent the chief branch  $ARDPB$  ( $T=f(x)$ ), corresponding with  $ASDQB$  ( $T=f(x')$ ), and also the four rudimentary parts.

	$x$	$x'$	$T$
(A)	0	0	1200
	0.477	0.05	749
	0.882	0.1	391
(R)	0.958	0.127 (S)	292
	0.929	0.2	335
	0.886	0.3	384
	0.846	0.4	419
	0.810	0.5	442
	0.780	0.6	454
	0.756	0.7	458 <sup>3</sup>
(D)	0.749	0.749	458 <sup>62</sup>
(P)	0.748	0.776 (Q)	458 <sup>60</sup>
	0.749	0.8	461
	0.795	0.9	465
	0.867	0.95	476
	0.911	0.97	484
	0.967	0.99	494
(B)	1	1	500

	$x$	$x'$	$T$
(A')	1	0 (B')	0
	0.995	0.05	193
(R')	0.981	0.104 (S')	245
	0.995	0.120	193
(D')	1	0.130 (E)	0

	$x$	$x'$	$T$
(B')	0	1 (A')	0
	$e^{-57.7}$	0.9997	16 <sup>5</sup>
(P')	$e^{-37}$	0.990 (Q')	25 <sup>9</sup>
	$e^{-57.6}$	0.970	16 <sup>5</sup>
(B')	0	0.954 (F)	0

For the exact calculations, of which these tables give the results, we refer to the more elaborate paper which will appear later. Also the figures relating to them are to be found there.

The maximum  $D$  has been calculated from the equation (9), which yields  $x = x' = \underline{0.7494}$ ,  $T = \underline{458^{\circ}62}$ .

The points  $P$  and  $Q$ , etc. are calculated from (6) in connection with  $\frac{\partial^2 \xi'}{\partial x'^2} = 0$ , or  $T = q_1 \beta' x' (1 - x')$ . We find the following *four* solutions:

I	$x' = 0.7762$ (Q)	$x = 0.7484$ (P)	$T = 458^{\circ}60$
II	$x' = 0.1268$ (S)	$x = 0.9579$ (R)	$T = 292^{\circ}3$
III	$x' = 0.9901$ (Q')	$x = e^{-37}$ (P')	$T = 25^{\circ}9$
IV	$x' = 0.1035$ (S')	$x = 0.9808$ (R')	$T = 245^{\circ}9$

The points  $E$  and  $F$  are again determined by (10) and (10a). For  $E$  we have ( $x = 1, T = 0$ )  $x' = \underline{0,1296}$ ; for  $F$  ( $x = 0, T = 0$ )  $x' = \underline{0,9535}$ .

Combining equation (6) for  $x_1'$  and  $x_2'$ , we find finally for the eutectic point  $C$ :

$$x = \underline{0,80673}; x_1' = \underline{0,08893}; x_2' = \underline{0,91107}; T = \underline{466^\circ,41}.$$

Formerly, when  $x'$  could be neglected, we have found from (8),  $x = 0,809, T = 452^\circ$  (see IV).

It is remarkable that the value found for  $x_2'$  is exactly equal to  $1 - x_1'$ . It is easy to show that this is an immediate consequence of the equations (6) (compare our previous paper).

In cases however in which our assumption  $\alpha_1' = \alpha_2'$  (which follows from  $b_1' = b_2'$ ) is not satisfied, the value of  $x_2'$  for the eutectic point will also not be equal to  $1 - x_1'$ .

*When the amount of heat required for the mixing of the first component for  $x = 1$  is equal to that of the second component for  $x = 0$ , then the compositions of the two solid phases at the eutectic point will be complementary.*

VII. We shall now discuss the question, how the two parts ending in the cusps  $P$  and  $R$  will gradually disappear. We may follow this process step by step in the following figures.

a) In fig. 10 we see that the cusp  $P$  of the line  $T = f(x)$ , which till now was situated *inside* the curve  $\frac{\partial^2 \bar{S}}{\partial x'^2} = 0$ , has *reached* that curve, in consequence of which the point  $Q$  of the line  $T = f'(x')$  coincides with  $P$ , and also with the maximum point  $D$ , which lies between  $P$  and  $Q$ . The curves  $T = f(x)$  and  $T = f'(x')$  run therefore both *horizontally* in  $P$ , and henceforth the curve  $T = f'(x')$  will no longer touch the branch  $RP$  in  $D$ , but the branch  $PB$  (in a *minimum*). After the horizontal position in fig. 10 the cusp at  $P$  will be turned *upwards* instead of downwards.

This transformation is apparently determined by the relations  $x = x'$ .  $\frac{\partial^2 \bar{S}}{\partial x'^2}$ , i. e. by

$$T = T_1 (1 - \beta' x^2) = T_2 \left( 1 - \frac{q_1}{q_2} \beta' (1-x)^2 \right) = q_1 \beta' x (1-x) \dots \quad (13)$$

This yields with the values assumed for  $T_1$  etc.:

$$\beta' = \underline{1,0611} \quad ; \quad x = \underline{0,7606} \quad ; \quad T = \underline{463^\circ,5}.$$

b. The figures 11 and 12 show a *second* peculiarity of the tran-

sition. Here the cusp  $P$  lies at the same height as  $C$ ; we find therefore at the temperature of the eutectic point for the first time four values of  $x'$ :  $x_1'$  and  $x_2'$  corresponding to  $C$ , and the coinciding points  $x_3'$  and  $x_4'$  corresponding to  $P$ . These latter two points still represent *unstable* conditions. A moment later  $P$  has risen above  $C$  and the two coinciding points  $x_3'$  and  $x_4'$  have separated (fig. 12). The values  $x_1'$  and  $x_2'$  always correspond to  $C$ ,  $x_3'$  and  $x_4'$  to two other points of the line  $T=f(x)$ . The phase to which  $x_3'$  relates, is *unstable*, that to which  $x_4'$  relates *metastable*.

The transition of fig. 11 is determined in combination of (6) for  $x_1'$  and  $x_2'$  (with  $x_c$ ), for  $x_3'$  (with  $x_p$ ), in connection with the relation  $T=q_1\beta'x_3'(1-x_3')$ . By means of these relations we may determine  $T, x_c, x_p, x_1', x_2', x_3', \beta'$ , if we moreover take into account  $x_2' = 1 - x_1'$  (compare VI above).

c. The figures 13 and 14 represent a new and very important case of transition. Formerly the branch  $AR$  intersected the branch  $BP$  always *on the left* of the maximum (or minimum)  $D$  in the eutectic point  $C$ ; in fig. 13 it passes *exactly through the point D*. From this follows, that the point  $x_4'$  coincides in  $C$  with  $x_2'$  (both  $=x$ ), which point represents a *stable* phase from this moment. Afterwards the minimum  $D$  lies *on the left* of the eutectic point  $C$  (see fig. 14) in consequence of which *the realizable part* of the meltingpoint curve begins to show *a totally different shape*, namely *with a minimum* (see fig. 14a). The point  $x_2'$  which till now lay *on the left* of  $C$ , lies in future *on the right* of that point. On the other hand  $x_4'$  has got on the left of  $C$  and it corresponds to a point of the line  $T=f(x)$  between  $B$  and  $D$ .

It will not escape our notice that the case drawn in fig. 14a occurs to some extent in the mixtures of  $\text{AgNO}_3$  and  $\text{NaNO}_3$ , investigated by Mr. HISSINK (see fig. 14b). The difference is only that the minimum  $D$  in the line  $T=f(x)$  in the case of fig. 14b appears beyond  $x=1$  and has therefore already disappeared. In our case we have supposed this to occur in a later stage.

The case of transition of fig. 13 is calculated from the equations (6) for  $x_1'$  and  $x_2'$ , taking into account  $x=x_2'$ , and moreover  $x_2' (=x_4') = 1 - x_1'$ . The numerical solution of these equations yields the following values:

$$\beta' = \underline{0,9247} ; x_1' = \underline{0,1940} ; x_2' = x_4' = x_c = \underline{0,8060} ; T = \underline{479^\circ,1}$$

We may then calculate  $x_3'$  and  $x_3$  from equation (6).

d. Finally the figures 15 and 16 represent the most important case of transition.

Here  $Q$  and  $S$  coincide with the summit of the curve  $\frac{\partial^2 \mathfrak{S}}{\partial x'^2} = 0$ , and so also,  $P$  and  $R$  with  $C$ . The parts with the cusps have now disappeared once for all through the eutectic point.

The points  $x_1'$ ,  $x_3'$  and  $x_2'$  coincide with the *horizontal* tangent in the *point of inflexion*  $Q,S$ . This point  $Q,S$  lies apparently at  $x' = \frac{1}{2}$ , as the curve  $\frac{\partial^2 \mathfrak{S}}{\partial x'^2} = 0$  or  $T = q_1 \beta' x' (1-x')$  is perfectly symmetrical on either side of the summit at  $x' = \frac{1}{2}$  according to our supposition  $a_1' = a_2'$  (in consequence of  $b_1' = b_2'$ ).

Not before this instant we may say that the meltingpoint curve has obtained a perfectly normal course, running continuously without any cusp from  $A$  to  $B$  with a *minimum* in  $D$  where  $x = x'$  (fig. 16). The point of inflexion with a horizontal tangent has passed into an ordinary point of inflexion with an oblique tangent. This point of inflexion also will gradually disappear when  $\beta'$  continues to diminish, and for still smaller values the minimum also will disappear from the meltingpoint line which will then show a continuously ascending course from  $B$  to  $A$ . It is of course possible that the minimum has disappeared already before, of which fig. 14*b* gives an example.

The transition of fig. 15 is determined by the equations (6) for  $x' (x_1' = x_2' = x_3') = \frac{1}{2}$ , in connection with  $\frac{\partial^2 \mathfrak{S}}{\partial x'^2} = 0$  or  $T = \frac{1}{4} q \beta'$ .

We find:

$$\beta' = \underline{0,8226} \quad ; \quad x = \underline{0,8030} \quad ; \quad T = \underline{492^\circ,6} \quad . \quad (x_1' = x_2' = x_3' = 0,5).$$

The points  $x_4'$  and  $x_4$  may further be calculated from equation (6).

e). The *minimum disappears* apparently (see III equation (5*bis*), when

$$\beta' \leq \frac{T_1 - T_2}{T_1} \quad . \quad (14)$$

For with  $\beta = 0$  formula (5 *bis*) passes into  $-\beta' < \frac{T_2 - T_1}{T_1}$

or  $\beta' > \frac{T_1 - T_2}{T_1}$ . This formula expresses the condition for the occurrence of a minimum. Formula (14) expresses consequently that *no* minimum will occur.

The minimum disappears therefore in our case as soon as  $\beta'$  becomes equal to  $\frac{7}{12}$  or 0,5823.

f). In the above considerations we have lost sight of the rudimentary pieces which have been detached (compare VI).



We shall now investigate when they also disappear. Apparently this is the case, when the summits  $P'$  and  $Q'$ ,  $R'$  and  $S'$  lie at  $T=0$ ; i.e. when these points coincide with  $B'$  and  $A'$ . These summits are determined by the equations (6), in connection with  $T=q_1 \beta' x' (1-x)$ . Now  $P'$  coincides with  $B$  and  $Q'$  with  $A$ , if these equations are satisfied by  $T=0$ ,  $x=0$ ,  $x'=1$ . It is clear that this requires  $\beta'=1$ . Further  $R'$  coincides with  $A'$  and  $S'$  with  $B'$ , if the equations are satisfied by  $T=0$ ,  $x=1$ ,  $x'=0$ . And this can only be the case when  $\beta' = \frac{q_1}{q_2}$ , in our case  $\beta' = \frac{5}{6} = \underline{\underline{0,8333}}$ .

VIII. It is easy to see that the results of the above investigation would remain unchanged *qualitatively*, if we had not neglected the quantity  $v$  in the term  $ax^2$ , and if we had not omitted the quantity  $\beta$  for the liquid phase by the side of the corresponding quantity  $\beta'$  ( $\beta$  being nearly always very small compared with  $\beta'$ ). Then all the values given for  $\beta'$ ,  $x$ ,  $x'$  and  $T$  would be slightly changed *numerically*, but the transformations and transitions which we have discussed, would have occurred in the same order and exactly in the same way as we have described above.

We conclude from the above considerations, that the occurrence of a *eutectic* point and the *apparent* interruption in the series of the solid mixtures caused by it, necessarily follow from the theory represented by the equations (2) or (6), which teaches that high values of  $\beta'$  (or  $a'$ ), i. e. of the heat required for the mixing of the solid phase, cause the occurrence of *unstable* conditions. In reality the curve is *continuous*, as is shown in the different figures, but in general only *a part* of the continuous meltingpoint-curve is liable to be realized. And only *this* part of course is found by means of the experiments.

Finally I regard it as an agreeable duty to express my thanks to Prof. BAKHUIS ROOZEBOOM, who has encouraged me to undertake this investigation, and who has given me many a useful hint also for my former papers on the meltingpoint-curves of amalgams and alloys.



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday September 26, 1903.

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Afdeling van Zaterdag 26 September 1903, Dl. XII).

CONTENTS.

A. SMITS: "The course of the solubility curve in the region of critical temperatures of binary mixtures". (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 171.

PH. VAN HARREVELD: "On the penetration into mercury of the roots of freely floating germinating seeds". (Communicated by Prof. J. W. MOLL), p. 182. (With one plate).

JAN DE VRIES: "The harmonic curves belonging to a given plane cubic curve", p. 197.

A. F. HOLLEMAN: "Preparation of cyclohexanol", p. 201.

TH. WEEVERS and Mrs. C. J. WEEVERS—DE GRAAFF: "Investigations of some xanthine derivatives in connection with the internal mutation of plants". (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 203.

J. VAN DE GRIEND JR.: "Rectifying curves". (Communicated by Prof. J. CARDINAAL), p. 208. (With one plate).

J. BOEKE: "On the development of the myocard in Teleosts". (Communicated by Prof. T. PLACE), p. 218. (With one plate).

Extract from a letter of Mr. V. WILLIOT to the Academy, p. 226.

The following papers were read:

**Chemistry.** — "*The course of the solubility curve in the region of critical temperatures of binary mixtures*"<sup>1)</sup>. By Dr. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

The results of the experiments on critical temperatures of binary mixtures, which have been suggested by the theory of VAN DER WAALS, and the completion of the pressure-temperature-concentration-diagram for the equilibrium of *solid* phases with liquid and vapour lately given by BAKHUIS ROOZEBOOM<sup>2)</sup>, made it probable that the pending

<sup>1)</sup> My first communication on this subject appeared in Zeitschr. f. Elektroch. 33, 663 (1903).

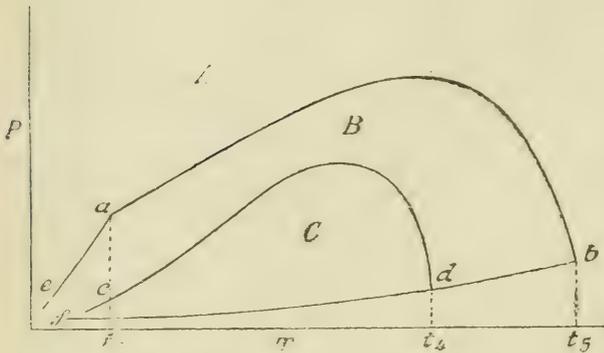
<sup>2)</sup> Proc. Royal Academy Amsterdam 1902, 276.

problem of the course of the solubility curve of a solid in the region of critical temperatures was now capable of solution.

It follows namely from the combination of the two conceptions mentioned above, that the course of the solubility curve cannot show anything remarkable, unless the least volatile substance (*B*) occurs as a solid phase and its melting point lies higher than the critical temperature of the more volatile substance (*A*), which for the sake of brevity we shall call solvent.

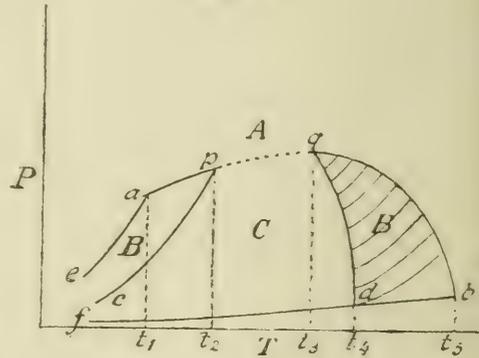
We will now consider only the case when the two substances in the liquid state are miscible in all proportions. Then there is in the  $p, t, v$ -diagram a continued critical curve, connecting the critical points of the two components. Three different cases may now occur.

Fig. 1.



*A* = Gas.  
*B* = Unsaturated solutions.  
*C* = Supersaturated solutions or solid *B* + vapour.

Fig. 2.



*A* = Gas.  
*B* = Unsaturated solutions.  
*C* = Supersaturated solutions or solid *B* + vapour.

Fig. 1 and 2 are  $p, t$ -projections of the representation in space, *a* is the critical point of *A*, *b* of *B*, while *d* represents the melting point of solid *B*. The line *ab* is the critical curve and *cd* the  $p, t$ -line for the three-phases equilibrium: solid *B*+solution+vapour. Further *ea* is the vapour-tension line of liquid *A*, *fb* that of liquid *B*.

Now the case of fig. 1 will occur when the solubility of solid *B* in *A* is comparatively great. In this case the vapour-tensions of the saturated solutions are rather small and so the curve *cd* lies totally below the critical curve.

The line *cd* runs on uninterruptedly as far as the melting point of *B*; the series of the saturated solutions of *B* is not interrupted by the critical phenomena of the solution; the solubility curve shows nothing remarkable. On the other hand the critical curve also goes on uninterruptedly, the critical phenomena being only those of solutions which are *unsaturated* of solid *B*.

In the second case, fig. 2, I supposed the solubility of  $B$  in  $A$ , even at the critical temperature of  $A$ , to be still so small, that just a little above it the line  $cd$  intersects the critical curve. Then such an intersection takes place in two points  $p$  and  $q$ .

Now the critical temperatures and pressures between  $a$  and  $p$  and between  $q$  and  $b$  refer to *unsaturated* solutions. At  $p$  and  $q$ , however where the  $p, t$ -line of the solutions and vapours saturated of solid  $B$  and the critical curve meet, the case occurs, when the saturated solution is found at its critical temperature; for here the vapour-tension of the saturated solution is quite equal to the critical pressure and so *saturation temperature and critical temperature must coincide*.

If we were to prolong the critical curve from  $p$  to  $q$ , we should pass through the region of solutions and vapours *supersaturated* of solid  $B$ . Hence critical phenomena will be possible here only provided that the solid phase  $B$  does not occur. So this part of the critical curve is *metastable*.

To prolong the three-phases-line between  $p$  and  $q$ , on the other hand, is impossible, as will soon be evident.

A third case forming a transition between fig. 1 and 2 would be the following: the curve  $cd$  would touch the inside of the critical curve in one point. The points  $p$  and  $q$  would coincide at this point. Hence the chance that such a case should occur is extremely small.

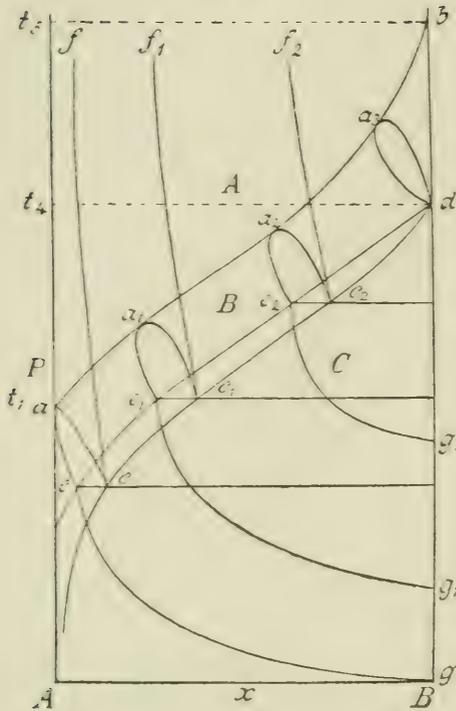
A better insight than by the  $p, t$ -projections of the representation in space is, however, given by the  $p, v$ -projections, especially when these are combined for different temperatures as in fig. 3 and 4, which has already been indicated by Prof. BAKHUIS ROOZEBOOM<sup>1)</sup>. That is why I here add  $p, v$ -projections both for case 1 and for case 2 and in order to be able to construct from these projections the entire  $t, v$ -diagrams also, I have given the projections starting from the critical temperature of  $A$  up to the melting point of  $B$ .

The preceding  $p, v$ -diagrams 3 and 4 correspond with the  $p, t$ -diagrams 1 and 2. Let us first confine ourselves to fig. 3. At the critical temperature  $t$  of the substance  $A$ ,  $ae$  and  $ac$  are the  $p, v$ -curves for coexisting vapours and liquids (unsaturated solutions). The points  $e$  and  $c$  indicate the *saturated* solution and the vapour in equilibrium with it. Further for the same temperature  $ge$  is the  $p, v$ -curve for the *vapours* and  $cf'$  the  $p, v$ -curve for the *solutions* coexisting with solid  $B$ . According to the theory of VAN DER WAALS  $ge$  and  $cf'$  are at bottom two portions of a *continuous curve*, which

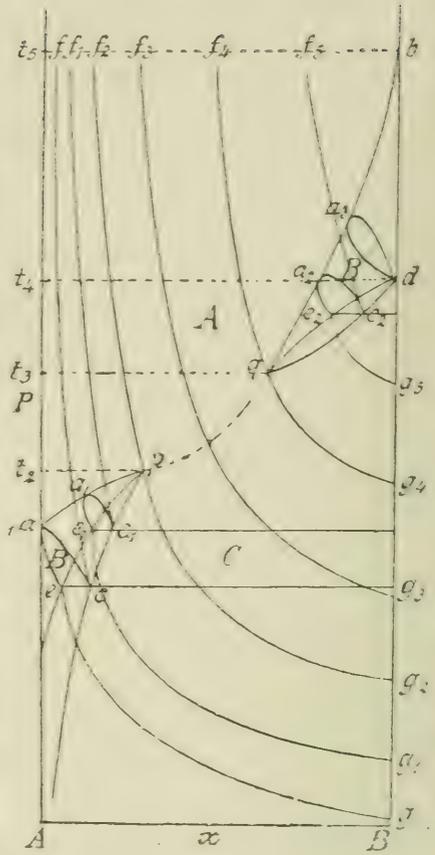
<sup>1)</sup> Zeitschr. f. Elektroch. **33**, 665, (1903).

Fig. 4.

Fig. 3.



$A$  = Gas.  
 $B$  = Unsaturated solutions.  
 $C$  = Supersaturated solutions or solid  $B +$  vapour.



$A$  = Gas.  
 $B$  = Unsaturated solutions.  
 $C$  = Supersaturated solutions or solid  $B +$  vapour.

has between  $c$  and  $e$  a part only partly to be realized with a maximum and a minimum.

For a somewhat higher temperature the diagram is a little different, because now the vapour- and liquid curve continuously pass into each other with a critical point in  $a_1$ , the vapour-line  $g_1c_1$  being shorter than at the former temperature. At rise of temperature this vapour-line continually decreases in length, until at the melting point of  $B$  in the point  $d$  it has disappeared altogether. Above the melting point a saturated solution is no longer possible and so there we get only a liquid- and a vapour-line with a critical point in  $a_2$ . If we draw a line through the points  $a, a_1, a_2, a_3$  and  $b$ , a second through the points  $c, c_1, c_2$  and  $d$  and a third through the points

$e$ ,  $e_1$ ,  $e_2$  and  $d$ , these lines indicate the said  $t, x$ -projections;  $ab$  is the critical curve,  $cd$  the curve of the saturated solutions and  $ad$  that of the vapours saturated with  $B$ . In accordance with fig. 1 the whole of the critical curve lies above the solubility curve; above the critical curve lies the gas-region and below the solubility curve the region of solid  $B$  + vapour or of the *supersaturated* solutions.

After what precedes the connection between the fig. 2 and 4 is easy to see.

The solubility of  $B$  in  $A$  at the temperature  $t_1$  being small, the vapour and liquid-lines  $ae$  and  $ac$  are short. Above  $t_1$   $ae$  and  $ac$  again fluently pass into each other and have already approached nearer to each other, because the saturated solution  $e_1$  and the coexisting vapour  $e_1$  differ less from each other; a consequence of this is that the lines  $g_1 e_1$  and  $e_1 f'_1$  have also approached to each other. At  $t_2$ , the first critical temperature of the saturated solution, the solubility curve  $ec_1 p$ , the vapour-line  $ee_1 p$  and the critical curve  $aa_1 p$  concur. This implies that at this temperature the curve  $g_2 p$  for the vapour coexisting with solid  $B$  is the prolongation of the curve  $pf'_2$  for the solution coexisting with solid  $B$ . The same occurs at a great many higher temperatures.

That a continuation of the lines  $ep$  and  $ep$  is *imaginary*, clearly appears from this diagram, as the vapour- and the liquid-line, if both were prolonged, would change places, which is impossible.<sup>1)</sup>

Whereas from  $t_2$  to  $t_3$  *saturated* solutions are absolutely impossible, at  $t_3$  the same phenomenon occurs as at  $t_2$ ; here also the solubility curve  $de_2 q$ , the vapour-line  $de_2 q$  and the critical curve  $ba_3 a_2 q$  converge and the critical phenomenon is observed with a *saturated* solution.

At higher temperatures a convergence of the three curves can no longer occur and in consequence all critical temperatures between  $t_3$  and  $t_5$ , just as between  $t_1$  and  $t_2$ , are critical temperatures of *unsaturated* solutions. If between  $p$  and  $q$  solution + vapour + solid  $B$  be impossible, it is conceivable, as suggested before, that we may succeed in getting *supersaturated* solutions and observing their critical phenomena. In such a case the dotted critical curve if prolonged might be realized between  $p$  and  $q$ , so this dotted line is *metastable*.

For a thorough knowledge of the phenomenon a  $p, x, t$ -diagram is most desirable and a  $v, x, t$ -diagram indispensable. Both space-

<sup>1)</sup> In the first communication, Zeitschr. f. Elektr. 33, 663, this point was not sufficiently cleared up.

representation I hope to communicate after some time and now I want to point out only the fact, that the point  $p$ , which is bound to a certain concentration can be reached at only one very definite volume, which holds true for  $q$  also.

By means of the  $v, x, t$ -diagram it can also be made clear, that no line can be drawn of a definite limitation between the region for solid  $B +$  vapour and the region of unsaturated vapours. In the region for solid  $B +$  vapour we have namely a system consisting of two components in two phases, therefore a bivariant system wherein there are numberless ways in which with rise of temperature the pressure can be changed. Consequently it depends altogether on the volume what course we follow at increase of temperature.

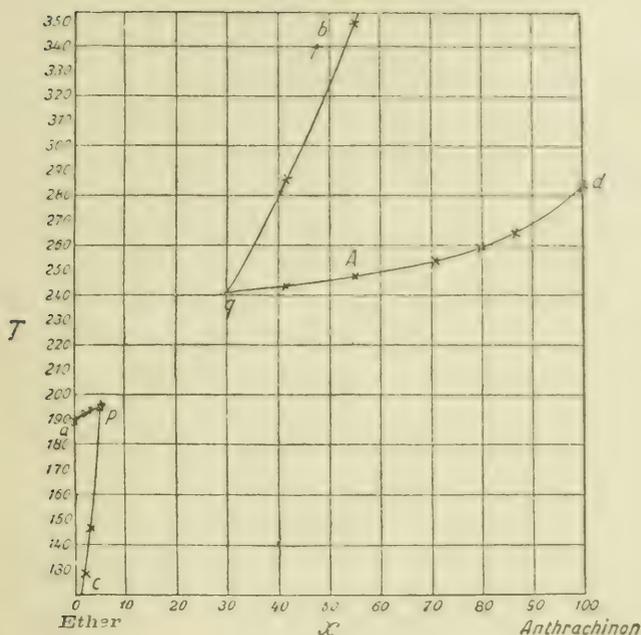
In order to test the discussed phenomena by an example I chose for the substances  $A$  and  $B$  ether and anthrachinon. The critical temperature of ether is  $190^\circ$ , hence it is rather low, nor is the critical pressure high, namely  $\pm 36$  atmospheres. It is obvious that these two circumstances make the experiment much easier. Anthrachinon was chosen because this substance is very little soluble in ether, its melting point lies  $283^\circ$  above the critical temperature of ether and it is still very stable at its melting point.

The experiments were carried out in thick-walled tubes of 5 c.m. length filled with weighed quantities of ether and anthrachinon. The ether was free from alcohol and water; the anthrachinon was crystallized from icevinegar. The tubes filled with ether and anthrachinon were closed by melting while in a bath of  $-80^\circ$  (solid  $\text{CO}_2 +$  alcohol) and then hanged up in an air-bath with little mica windows. This air-bath had been supplied with an apparatus, driven by a motor, for keeping the tubes constantly swinging. The temperature of the bath could be kept constant within  $1^\circ$ .

In order to determine the solubility curve the temperature was observed at which all the anthrachinon had been dissolved. In order to determine the critical curve at very slow decrease or increase of temperature this was noted down when formation of nebula occurred, resp. the liquid phase disappeared. The average of the two temperatures was noted down in the graphical representation. If possible the volume of the liquid was chosen in such a way, that on reaching the critical temperature the tube was nearly filled with liquid. Only saturation- and critical temperatures for mixtures of definite concentration being determined by these experiments, only a  $t, v$ -diagram can of course be constructed from them, which is given in fig. 5.

From a comparison with fig. 4 it is easy to see that the direction of the two pieces of the critical line and that of the line for the

Fig. 5.



solutions saturated with solid *B* is quite conformable with the *t*, *x*-projection in fig. 4. The point *p* lies at  $195^{\circ}$ , 95% ether and 5% anthrachinon. The point *q* has, as regards the concentration, not yet exactly been determined; I estimate it at 70% ether and 30% anthrachinon, the temperature lies at  $241^{\circ}$ .

In order to elucidate the very remarkable phenomena we found, I shall more closely consider the case that we start from a mixture of ether and anthrachinon composed of 45% ether and 55% anthrachinon (*A* fig. 5) and slowly heat this mixture. The quantity of anthrachinon being so great and the volume rather small, we always have below  $195^{\circ}$  excess of solid anthrachinon together with a saturated solution and vapour. The concentration of the saturated solution at rise of temperature moves along the line *cp*. At about  $195^{\circ}$  we reach the first critical temperature of the saturated solution, when more heat is added the solution disappears and we get solid anthrachinon + vapour. Apart from the continually increasing evaporation of anthrachinon all remains unchanged up to about  $241^{\circ}$ . At this temperature the critical phenomenon occurs again; whereas at *p* the liquid phase disappeared, here it is formed again<sup>1)</sup>. On further rise of temperature more anthrachinon is continually dissolving and along

<sup>1)</sup> The points *p* and *q* can never be accurately reached in one experiment, a very definite volume being required for every concentration.

$qd$  we go to the point  $A$ , where at  $247^\circ$  all anthrachinon has exactly been dissolved. If we now increase the temperature still more we come into the region of *unsaturated* solutions; from  $A$  therefore, we go parallel to the  $T$ -axis upwards to the temperature  $350^\circ$ , where the *unsaturated* solution has reached its critical temperature and all passes into the gaseous state.

The influence, which greatly diminishes the accuracy of the results, is the dependency of the volume; the error created by it, is small for the critical curve  $ap$  and for the solubility curve  $bq$ , because these curves have a rather slight curvature. For the critical curve  $bq$  and especially for the lower part the possible error in the concentration is rather great, so that the point  $q$  is pretty uncertain.

It seemed very interesting to me to investigate, whether or not it would be possible to determine points of the metastable part of the critical curve. I indeed succeeded to get between the temperatures  $t_2$  and  $t_3$  a solution, which, as discussed before, was supersaturated. A tube filled with 6% anthrachinon and 94% ether was heated in the air-bath. The solution saturated at the first critical temperature containing only 5% anthrachinon, some solid anthrachinon was still left above the critical temperature of  $195^\circ$ . At increase of temperature always more anthrachinon passed into vapour and at last all had become gas. Now, if I made the temperature fall rather quickly, no solid anthrachinon was deposited, which would have been normal, but at  $211^\circ$  a nebula appeared and a *supersaturated solution* was formed. Then, when I made the temperature fall slowly, the solution remained over a range of temperature of  $9^\circ$ . At  $202^\circ$  suddenly a transformation appeared by which the solution passed into solid anthrachinon and vapour and the metastable phase disappeared. On subtracting more heat the formation of nebula once more appeared at  $\pm 195^\circ$ , the first critical temperature of the saturated solution, and for the second time a liquid was formed, but now this liquid was a stable phase. This phenomenon shows, that vapours are also possible, which are *supersaturated of solid* and for their transition into the stable phase choose a round-about way by another metastable phase, viz. a supersaturated solution.

I repeated the same experiment with a greater anthrachinon-concentration; now the formation of nebula appeared at  $216^\circ$ , it is true, but before a visible quantity of liquid had been formed, solid anthrachinon already was deposited. These two temperatures could not serve to determine the metastable part of the critical curve, because the vapour-space in the tube happened to be too large. So the temperatures under observation were not critical temperatures.

The results obtained enable me to somewhat elucidate a few dark points occurring in literature. From the experiments of WALDEN and CENTNERSZWER<sup>1)</sup> on the solubility of KJ in liquid  $\text{SO}_2$  up to  $96^\circ$ , it is obvious that after one of the two liquid layers, which are coexistent between  $77^\circ.3$  and  $88^\circ$ , have disappeared, the solubility decreases and at  $96^\circ$  amounts to no more than 0,58 mol. % KJ.

On account of this in their diagram they make the solubility curve below  $100^\circ$  terminate into the  $t$ -axis, as indicated in fig. 6. It is obvious, that this is not compatible with the theory given above, the prolonging of the solubility curve as far as the  $t$ -axis is certainly wrong. Most probably the same phenomenon appears with  $\text{SO}_2$  and KJ as with ether and anthrachinon; the diagram may be somewhat different, the type, however, will be the same<sup>2)</sup>. Hence it is not improbable, that on prolonging the solubility curve up to higher temperatures we should again observe an increase of the solubility, so that the direction up to the first critical temperature of the saturated solution will be somewhat like that indicated in fig. 7.

Fig. 6.

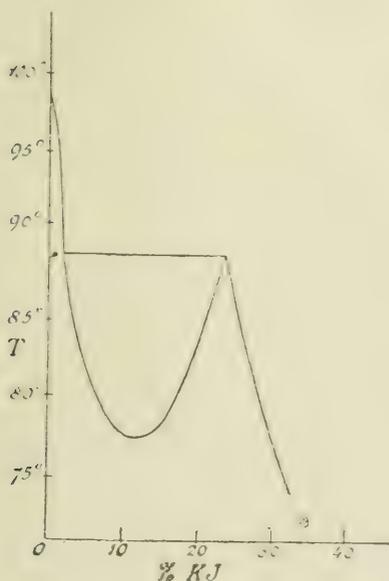
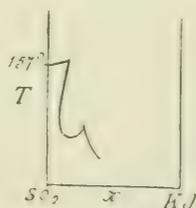


Fig. 7.



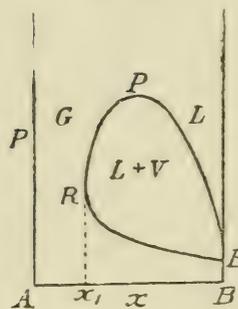
Since 1880 many more experiments have been made which point to the fact, that gases above their critical state are able to dissolve

<sup>1)</sup> Zeitschr. f. physik. Chem. **42**, 456 (1903)

<sup>2)</sup> For the systems  $\text{SO}_2 + \text{RbJ}$  and  $\text{SO}_2 + \text{NaJ}$  the same holds true. Zeitschr. f. physik. Chem. **39**, 552 (1902).

liquids and solids<sup>1)</sup>. VILLARD e. g. found, that when he compressed oxygen at the usual temperature ( $17^\circ$ ) to  $\pm 200$  atmospheres in a tube with bromine, this evaporated in a much higher degree than corresponded with the vapour-tension at the temperature of observation. This could be observed because, while the oxygen was being compressed, the colour of the vapour grew darker and darker and because bromine on decrease of pressure was deposited against the wall in the form of little drops.

Fig 8.



Prof. BAKHUIS ROOZEBOOM<sup>2)</sup> has already given an explanation of this phenomenon by means of the  $p$ - $x$ -loop, which applies to the said system of oxygen—bromine at  $17^\circ$ , because this temperature lies far above the critical temperature of oxygen ( $-111^\circ$ ) and also above the melting point of bromine ( $-7,3^\circ$ ).

According to HARTMANN<sup>3)</sup> this  $p$ - $x$ -loop has the form, given in fig. 8. It follows from the great rise and running back of the vapour-line  $ERP$ , that the partial pressure of the vapour of  $B$  between  $R$  and  $P$  must be much greater than the pressure in  $E$ . Though increase of pressure alone is sufficient to increase the vapour-tension, the influence of compressed gases is much greater in consequence of the solution of the gas in the liquid.

It is clear that by increase of the oxygen-tension *total* evaporation can be reached here, the region liquid + vapour having for a certain concentration of  $A$  given place to the gas-region.

With the systems  $\text{CH}_4$ — $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{CH}_4$ — $\text{CS}_2$ ,  $\text{CH}_4$ — $\text{C}_2\text{H}_5\text{OH}$  VILLARD found the same phenomenon in an even more striking way. Also with *solids* VILLARD could observe an increase of the partial pressure. The partial pressure of iodine was perceptibly increased by an oxygen-pressure of  $\pm 100$  atmospheres, whereas with hydrogen a perceptible increase did not occur until at 200 à 300 atmospheres. At  $\pm 300$  atmospheres methane dissolves very perceptible quantities of camphor and paraffine, even so much that on decrease of pressure the dissolved substances crystallize in visible quantities against the walls of the tube.

At 300 atmospheres ethylene dissolves rather much  $J$ , which on

1) HANNAY and HOGARTH. Proc. Roy. Soc. **30**, 178, (1880).

VILLARD. Journ. de Phys (3) **5**, 453 (1896).

WOOD. Phyl. Mag. **41**, 423, (1896).

2) Die Heterogene Gleichgewichte **2**, 99.

3) Journ. phys. Chem. **5** 425 (1901).

decrease of pressure is deposited in crystals. Paraffine strongly dissolves in aethylene; so much so that under a pressure of 150 atmospheres we can make it evaporate *altogether*. Stearine acid also easily dissolves in aethylene, but not to such a high degree as paraffine.

As yet we have not been able to explain the total evaporation of a solid by a gas above its critical state, *without an intermediate liquid phase*; this is owing to the fact, that there was no suspicion of the behaviour shown by the system ether and anthrachinon. If we compare the figures 3 and 4 with each other, it is obvious that if in fig. 3 we start from solid *B* and by compression of *A* at a constant temperature we follow a course parallel to the *x*-axis from right to left, a liquid phase will always appear first before we come into the gas-region. This phenomenon observed by VILLARD in the system camphor-aethylene will also occur in fig. 4 between the temperatures  $t_1$  and  $t_2$  and between  $t_3$  and  $t_4$ , so that this behaviour does not decide the type to which the system belongs. Investigations at different temperatures only would enable us to do so.

It is, however, quite different, when the solid evaporates altogether without giving a liquid first. If this be the case we can directly point out the type; then it belongs namely to type fig. 4, *for there only it is possible when coming from the region for solid B+vapour to pass into the gas-region without an intermediate liquid-phase, as long as we work between the temperatures  $t_2$  and  $t_5$ .*

Probably the systems alcohol + KI, KBr, Ca Cl<sub>2</sub> and CS<sub>2</sub> + I<sub>2</sub> of HANNAY and HOGARTH, ether + HgI<sub>2</sub> of WOOD and CO<sub>2</sub> + I<sub>2</sub> of VILLARD belong for the greater part to the type fig. 4.

That, as would follow from VILLARD's experiments, also the partial vapour tension of solids would be considerably increased by relatively slight pressures (100 à 200 atmospheres) of an additional gas, seems, however, possible to me only when the vapour-line of the system solid-vapour can get a course similar to that of liquid-vapour, which will probably be the case only when the added gas *A* dissolves in the solid phase *B*. This point will soon be investigated by me.

*Chemical laboratory of the University.*

*Amsterdam, September 1903.*

**Botany.** — “*On the penetration into mercury of the roots of freely floating germinating seeds.*” By PH. VAN HARREVELD. (Communicated by Prof. J. W. MOLL).

The first who mentioned that growing germroots can penetrate into mercury was JULES PINOT in 1829. He placed various seeds in a thin layer of water on mercury and observed that on germination a number of roots pushed themselves into the mercury.

His experiments were important in two respects. Firstly from a physiological point of view: the penetration of the germroots into a liquid of so high a specific gravity as mercury proved that during growth considerable forces are developed. And secondly from a physical point of view: the seeds lay loose and yet the germroots were not lifted out of the mercury by the upward pressure.

These two results of PINOT's experiments must be clearly distinguished. On the first much work has later been done; SACHS and other investigators used mercury repeatedly in order to give a great and uniform resistance to a downward growing root. On the second point, the physical paradox of the root which penetrates into mercury without a hold, no publication has appeared after that of WIGAND in 1854. PINOT himself was only struck by the second result of his experiment, the penetration of loose lying seeds. As this phenomenon could not be explained by physical laws, he called in the aid of vital force, as was still very common in his days.

The vitalistic doctrine however had found a fierce opponent in DUTROCHET<sup>1)</sup>. The latter declared the experiments to be untrustworthy. Several investigators, on the other hand, confirmed PINOT's observation. Thereupon DURAND and DUTROCHET gave, in 1845, an explanation of the curious fact which was generally accepted. Although WIGAND in 1854 assured once more that PINOT's observation was correct and still awaited an explanation, no further attention was paid to it. PINOT was often quoted for his first result; for the phenomena of freely floating seeds at best reference was made to the refutation by DURAND and DUTROCHET.

Reading the astonishment of WIGAND, when he was obliged to state the correctness of PINOT's observations, I repeated the experiments. I found that PINOT was right indeed. The explanation of the seeming physical paradox can nowadays be easily given; a “vital force” is not needed for it.

In the older literature on geotropic phenomena one meets with such contradictory opinions about the penetration of freely floating

<sup>1)</sup> J. SACHS, *Geschichte der Botanik* 1875. pag. 550.

seeds, that it may be useful to give a short synopsis of the literature on the subject. I shall afterwards compare the various opinions with the true explanation.

*Historical synopsis.*

On February 23, 1829, JULES PIXOT sent to the Paris Academy of Sciences a paper on the penetration of germroots into mercury. The Academy appointed a committee of three members to examine this paper.

PIXOT repeated his experiments in the "jardin du Roi" in the presence of two of the members of this committee. He also showed one member a new experiment, in order to guard his conclusions against possible objections. In a letter to the Academy, dated July 27, 1829, he gave a description of it. Neither the paper nor the letter seem to have been printed. But PIXOT published a short account of his first paper, together with an extract of his letter about the new experiment, in the *Revue Bibliographique* of July 1829<sup>1)</sup>.

According to this account he arranged his experiments in the following manner: a little trough, 18 mm. deep and 10 mm. broad was filled with mercury and a thin layer of water poured out on the mercury. The trough stood in a small dish with water over which a little bell-jar was placed. Seeds of *Lathyrus odoratus*, soaked in water, were placed on the mercury with the hilum turned towards the mercury surface.

The layer of water was sufficient to maintain germination, but was on the other hand, as thin as possible in order not to favour rotting of the seeds. Now on germination the roots of the freely floating *Lathyrus* seeds penetrated to a fairly considerable depth into the mercury without lifting the seed. Also with other seeds the experiment was successful; the penetration sometimes exceeded 8 or 10 mm. When however the growing little stem was killed by a drop of sulphuric acid, the root came to the surface.

<sup>1)</sup> *Revue Bibliographique pour servir de complément aux Annales des sciences naturelles*; par M. M. Audouin, Ad. Brongniart et Dumas. Année 1829 page 94—96.

This *Revue Bibliographique* only appeared in the years 1829, 1830 and 1831. With many specimens each of the three yearly volumes is bound with one of the three volumes which appeared annually of the *Annales des sciences naturelles*. As they have a separate pagination however, it is not sufficient to quote the number of the page and the volume of the *Ann. d. sc. nat.*, as HOFMEISTER (1860), GIESIELEKI (1872) and others do. A. P. DE CANDOLLE in his *Physiologie végétale* II. p. 828, note (1) calls this *Revue Bibl.* wrongly: *Ann. sc. nat.*, *Bull.* which may cause confusion with the "*Bulletin des sciences naturelles et de géologie*", which appeared from 1824 (T. I) till 1831 (T. XXVII).

In order to discover to what extent the weight of the seed and its adhesion to the moist mercury-surface could be the cause of this penetration, PIXOT devised the following experiment, described in the extract of his letter. A silver needle rested in the middle very movably on an axis. On one end a germinating Lathyrus seed was stuck, on the other end a movable pellet of wax, just balancing the seed. The seed hung about two millimetres above a moist mercury-surface; a bell-jar again kept the air moist. The germination now proceeded somewhat more slowly, but the root still reached the mercury-surface; next it forced itself into the mercury, as in the case of the unsupported seeds, without pushing the balance-arm upwards. For this experiment Lathyrus was chosen because with it the cotyledons remain within the coats of the seed. Neither could the weight cause the penetration as it was balanced by the wax-pellet and also adhesion between the cotyledons and the mercury was excluded as they did not touch each other.

PIXOT gave the facts as he observed them but he did not venture an explanation. That he would not have been averse to using the vital force for it, however, appears from the mention he makes of the sulphuric acid: as soon as he killed the germinating plant by it, the root came to the surface of the mercury.

PIXOT also communicated his discovery to the "Société de Pharmacie de Paris", which gave an extract of his letter in the Bulletin of the transactions of its meeting of August 15, 1829.<sup>1)</sup> The same article is found in Flora of that year<sup>2)</sup>, in the Edinburgh New Philos. Journal<sup>3)</sup> and in the Annalen der Gewächskunde<sup>4)</sup>.

These publications drew general attention, firstly because it appeared from them that roots grow downwards with great force and secondly because it remained unexplained how the seeds found a point of resistance against the upward pressure of the mercury. This latter point occupied more particularly PIXOT's countrymen, whereas some foreign workers were especially struck by the former. Among these CLAAS MULDER of Franeker repeated the experiments and gave a translation of PIXOT's article in the Revue Bibliographique together with the description of his own experiments in the autumn of 1829.<sup>5)</sup>

1) Journal de Pharmacie et des sciences accessoires, T. XV 1829 pag. 490—491.

2) Flora oder Botanische Zeitung, XII<sup>ter</sup> Jahrgang Zweiter Band 1829 pag. 687-688.

3) The Edinburgh New Philosophical Journal, July—October 1829 pag. 376—377.

4) Annalen der Gewächskunde, Bd. IV pag. 407—408.

5) Bijdragen tot de natuurkundige Wetenschappen, verzameld door H. C. VAN HALL, W. VROLIK en G. J. MULDER. Vierde deel 1829 pag. 428—437.

He took "small beer-glasses" of a little more than 5 cm. diameter (MULDER speaks of N. inches, i. e. new inches or centimetres) and filled them with mercury 4 cm. deep, on which lay a layer of water with pigeon-beans (*Vicia faba minima*) and buckwheat. The roots of buckwheat did not penetrate into the mercury and went on creeping over the surface for a month. When the beans had grown stems of two centimetres, five of them had their roots in the mercury: the rest lay on the surface but had evidently been submerged.

In order to prevent capsizing, a few of the seedlings of *Vicia* were picked out which had straight roots and these were stuck through holes in a thin slice of cork, floating on the water above the mercury. Especially between the wall of the glass and the mercury he now observed the penetration of the secondary roots.

His conclusion is that these experiments afford a new proof that the innate tendency of the root to grow downwards, must be considered as a vital action dependent upon internal force which external circumstances can hinder, modify and even render almost irrecognisable, but by no means destroy.<sup>1)</sup>

MULDER thinks only of the force with which the roots grow downwards. The physical paradox escapes his attention, although it was exactly this which was emphasised by PIXOT's experiment with the silver needle. By his using big seeds, seedlings in an advanced stage and cork, his experiments differ materially from those of PIXOT. A short account of MULDER's experiments by C. MORRIS appeared in the *Revue Bibliographique*; also in *Linnaea* there is an extract of his article.<sup>2)</sup>

H. R. GOEPPERT at Breslau repeated PIXOT's experiments as MULDER did, when he read an account of them in *Frouer's Notizen für Natur- und Heilkunde* Nr. 530, Aug. 1829, page 154. He described his experiments in an article, entitled: "Über das Keimen der Samen auf Quecksilber". GOEPPERT used peas and oats: only the primary roots of the peas made a small depression in the mercury, the other roots crept over the surface. Better than with PIXOT's silver balance he thought to eliminate the weight of the seeds by putting them into the holes of a wooden cross which above the mercury was held fast in a conically shaped glass. No more than MULDER he noticed PIXOT's physical paradox, for the friction of the seed in the

<sup>1)</sup> l. c. pag. 436.

<sup>2)</sup> *Revue Bibliographique*. Dec. 1830, pag. 129—130.

<sup>3)</sup> *Linnaea* Bd. 5, pag. 191 of the "Literatur-Bericht".

<sup>4)</sup> *Verhandlungen des Vereins zur Beförderung des Gartenbaues*, Vfter Band 1831, pag. 204—206.

holes of the wooden cross now counteracted the upward pressure of the mercury. GOEPPERT worked even with the bulb of a hyacinth!

It has been remarked above that in France it was exactly the unsupported condition of the seeds which drew attention because it seemed to plead for "vital force". DUTROCHET had commenced the great fight against this latter and consequently he was prompt to stave off the danger. He repeated PINOT's experiments and obtained a negative result. Thereupon, on Nov. 16, 1829, he made the following communication to the Académie des sciences, of which he was a corresponding member.<sup>1)</sup> "Par les journaux et particulièrement par les Annales d'expériences présentées à l'Académie"<sup>2)</sup> he had learnt that the roots of plants would penetrate into mercury to a greater depth than corresponded to their weight, consequently by a physiological action. He had repeated these experiments carefully but had by no means obtained the result of the author. The root never went deeper than it ought to by its weight and when after a few days it turned black and died, it did not come to the surface either. The author must be entirely mistaken; there was nothing that could be ascribed to physiological or vital action.

In this meeting of the Académie MIRBEL communicated that the committee of enquiry had also repeated the experiments, but had obtained the same result as DUTROCHET<sup>3)</sup>. This statement is contrary to what PINOT had said of the committee in his letter to the Académie of July 27, 1829. The committee has given no written report<sup>4)</sup>.

DUTROCHET evidently was no unprejudiced observer when he repeated PINOT's experiments. They were troublesome to the new conceptions of which he was a champion.

A considerable part of DUTROCHET's observations on various subjects

<sup>1)</sup> Revue Bibliographique. Dec. 1829, pag. 146—147.

<sup>2)</sup> A periodical of this name is not known to me. Only in 1835 the Académie began to publish a printed account of its meetings viz. the: Comptes Rendus hebdomadaires des séances de l'Académie des Sciences. Of its transactions, entitled: "Mémoires de l'Académie des Sciences de l'Institut de France", the new series was commenced as early as 1818, but not all the Mémoires that came in, are found in it. It contains an account of the proceedings of the Académie of some years; vol. XI 1832, has the account of 1828, vol. XVI 1838, that of 1830 and 1831, but exactly an account of 1829 is wanting in the intermediate volumes. Yet one reads in the "Analyse des travaux de l'Académie pendant l'année 1831" in Tome XVI 1838, page CCI: "Dans l'analyse des travaux de 1829, on a déjà donné une description...", from which would follow that the account for 1829 had been published.

<sup>3)</sup> Revue Bibl. Dec. 1829 p. 147.

<sup>4)</sup> Comtes rendus T. XX 1845 p. 1258.

has later been proved to be false. And in spite of all the praise which SACHS justly bestows on him, he adds that DUTROCHET "sich oft durch seine eigenen Vorurtheile beirren liesz" <sup>1)</sup>).

Meanwhile the question remained unsettled, for DUTROCHET gave only a negation and no explanation. On Dec. 9, 1829, he also read his article to the Société de Pharmacie de Paris <sup>2)</sup>).

In 1832 appeared the *Physiologie végétale* by A. P. DE CANDOLLE who gave a short description of the experiments of PINOT and MULDER <sup>3)</sup>. He wrongly was of opinion that PINOT fixed the seeds, for his silver needle was a movable balance. From MULDER's experiments he drew the conclusion that the roots penetrated into the mercury on account of their "stiffness"; the tender roots of the buckwheat were not stiff enough then to force themselves in. To the penetration of freely floating seeds he opposed DUTROCHET's negation.

Several handbooks of those days, as those of BISCHOFF, LINDLEY, TREVIRANUS and MEYEN, make no mention of the experiments with mercury. DUTROCHET himself omits them entirely from his "*Mémoires pour servir à l'histoire anatomique et physiologique des végétaux et des animaux*", 1837.

On May 27, 1844, however, PAYER sent a paper to the Académie, entitled "*Mémoire sur la tendance des racines à s'enfoncer dans la terre et sur leur force de pénétration.*" In this paper he described his experiments which seemed to confirm PINOT's observations. The paper itself does not seem to have been printed; an extract of it however was given by PAYER in the *Comptes Rendus* <sup>4)</sup>, while an elaborate report of it occurs in the *Comptes Rendus* of 1845 <sup>5)</sup>.

PAYER devised an apparatus in order to determine the depth to which a germroot could penetrate into the mercury. For this purpose he used layers of mercury of varying thickness, being at the bottom in contact with a layer of water. In a glass trough namely, one or

<sup>1)</sup> SACHS, *Geschichte der Botanik* 1875 p. 555.

<sup>2)</sup> *Journal de Pharmacie* Tome XVI 1830 p. 28.

<sup>3)</sup> A. P. DE CANDOLLE, *Physiologie végétale* Tome II 1832 p. 827—828.

<sup>4)</sup> *Comptes rendus* Tome XVIII. 1844 pag. 993—995. HOFMEISTER gives p. 933 instead of p. 993; this mistake is found in the following papers:

HOFMEISTER, *Ber. der kön. Sächs. Ges. d. Wiss. zu Leipzig* XII 1860 p. 203.

HOFMEISTER, *Pringsh. Jahrb.* III 1863 p. 105.

HOFMEISTER, *Die Lehre von der Pflanzenzelle* 1867 p. 284.

A. B. FRANK, *Beiträge zur Pflanzenphysiologie*, 1868 p. 22.

TH. CIESIELKI, in *Cohn's Beiträge zur Biologie der Pflanzen* I, 2 1872 p. 11.

A. SCHÖBER, *Die Anschauungen über den Geotropismus der Pflanzen seit Knight*, 1899 pag. 9.

<sup>5)</sup> *Comptes rendus* Tome XX 1845 p. 1257—1268.

more pieces of platinum gauze were fixed horizontally, on which a patch of muslin or cotton was placed. The trough was filled with water as high as the patch, in some experiments it contained oil or only air; then the mercury was poured on the patch. The tension of the lower mercury-surface was great enough to prevent the mercury from being forced through the meshes.

Now PAYER made various seeds germinate in the layer of water on the mercury. It will be presently seen that he fixed the seeds to some extent. Of some he saw the roots penetrate through a layer of mercury of as much as two centimetres and appear in the water under it. Of other seeds the roots remained creeping on the mercury, of others still they only penetrated a few millimetres. Hence PAYER concludes that the roots have a different penetrative power, not depending on differences of weight, stiffness or size. Weight alone cannot be the cause, for if the roots are taken from the mercury they do not sink in it again. They remain floating and only the growing part can penetrate again. Differences in stiffness cannot cause the varying behaviour, any more than differences in size. For roots of garden-cress (*Lepidium sativum*) do penetrate, those of buckwheat do not, although the latter are bigger, stiffer and heavier than the former.

Of the committee which had to report on this paper by PAYER, DUTROCHET (since 1831 an ordinary member of the Académie) was the reporter. The report was late in appearing and meanwhile on March 24, 1845, DURAND sent a paper to the Académie in which he thought to be able to reconcile the conflicting opinions.

DURAND says in the extract of his "Mémoire sur un fait singulier de la physiologie des racines"<sup>1)</sup> about the experiments of PINOT, MULDER and PAYER: "J'avais toujours vu là, au contraire, une de ces expériences trop légèrement faites et illégitimement imposées à la science, dont elles faussent ou paralysent les inductions: un fait à rayer des catalogues physiologiques." Therefore he wants to repeat these experiments and to give their normal explanation. He makes a clear distinction between loose and fixed seeds. He gives the following synopsis of the cases which can occur.

1. The seed is fixed above the mercury; the root then penetrates into the mercury perpendicularly to a depth of more than 4 centimetres.

2. The seed is loose. Here we have two cases:

A. It reaches the margin of the mercury-surface. Then the root

<sup>1)</sup> Comptes rendus Tome XX 1845 pag. 861—862.

forces itself between glass and mercury and is held fast by the lateral pressure of the mercury.

*B.* It stays in the middle. Here again two cases:

*a.* The mercurial surface remains pure. Then the root does not sink deeper than it should do on account of its weight.

*b.* A resistant, flexible layer is formed on the mercury, consisting of soluble matter of the seed which on evaporation of the water remains on the mercury. The root can then penetrate as this layer sticks the seed to the surface.

Case *a.* occurred in DUTROCHET's experiments and in those of the committee for PINOT's paper; case *b* is that of PINOT and MULDER. With MULDER buckwheat did not penetrate because it gave off little or no soluble matter to the water. So DURAND reduces all the cases of a penetration, greater than the weight, to the first-mentioned case, fixation of the seeds.

It appears from DUTROCHET's report that DURAND also speaks of "une adhérence capillaire entre la graine et la surface du mercure",<sup>1)</sup> which gives the seed some support for the penetration of the germroot when the layer of water has almost evaporated. It is not clear whether he means the evaporating layer of water or the resistant layer which he later uses for the explanation of the case under *b.*

On April 28, 1845, i. e. a month later, a combined report appeared on the papers by PAYER and DURAND. DUTROCHET was the reporter.<sup>2)</sup>

In the meantime it had become clear that PAYER had not distinctly felt the difference between experiments on germination upon mercury with loose and with partly fixed seeds. He had not mentioned namely in his *Mémoire* that his germroots were put through holes in a slice of cork or lay in cottonwool; not till later, on April 15, 1845, he had declared this to the committee. PAYER moreover declared that he had used the word "penetrative power" only in a superficial meaning, not involving a special vital force.

So PAYER's experiments were no longer alarming, especially now that DURAND had given an explanation of those of PINOT. For in these latter the seedling was stated to have stuck to the surface of the mercury, because on evaporation of the water a sticking-plaster was formed of soluble substances of the seed with mercury. In his report DUTROCHET says<sup>3)</sup>: "La couche dont il est ici question est une mixture avec le mercure des substances organiques qui ont été dissoutes dans l'eau." "Telle est selon M. DURAND, la cause de la

<sup>1)</sup> Comptes rendus Tome XX 1845 p. 1263.

<sup>2)</sup> Comptes rendus Tome XX 1845 p. 1257—1268.

<sup>3)</sup> Idem p. 1264.

pénétration de la radicule dans le mercure lorsque la graine est déposée sur la surface de ce métal couvert d'un peu d'eau; il faut que la graine soit agglutinée à la surface de ce métal par le moyen d'un enduit qui s'y forme pour que cette pénétration ait lieu. Lorsque le mercure conserve son poli, les radicules ne s'y enfoncent jamais au delà de ce qui est déterminé par la pesanteur des graines."

So the paradox had been subjected to known physical laws.

The matter seemed to be settled for good and all, when in 1854 once more an investigator confirmed PINOT's observations.

ALBERT WIGAND at Marburg wrote in his "Botanische Untersuchungen" a chapter, entitled "Versuche über das Richtungsgesetz der Pflanze beim Keimen" <sup>1)</sup>. He mentioned in it the experiments of PINOT, MULDER and DUTROCHET, without quoting the literature on the subject. He said that PINOT and MULDER fixed the seeds but that DUTROCHET let them free and hence obtained a negative result. <sup>2)</sup> Evidently he derived this erroneous idea about PINOT from RÖPER's translation of DE CANDOLE's *Physiologie végétale*.

WIGAND dared scarcely confess that he also had made seeds germinate when they floated on the mercury, so firmly was he convinced of the impossibility of success in this case. <sup>3)</sup>

But the result was undeniable, and so he nevertheless described his experiments.

The seedlings grew in a very thin layer of water on the mercury or on dry mercury in an atmosphere saturated with water-vapour. Some roots penetrated perpendicularly into the mercury as far as  $\frac{1}{2}$  "Zoll". <sup>4)</sup> Others grew in a slanting direction into the mercury or at first perpendicularly and then more horizontally or the apex came out of the mercury again or it grew horizontally at first and then perpendicularly downwards. A great number of roots remained creeping over the surface. Seedlings that had been taken out of the mercury could be replaced to the same depth. Along the glass wall many roots penetrated.

For seeds of smaller size than beans, weight was hardly a factor for the penetration; a seed of garden-cress made scarcely any depression in the mercury and yet the root penetrated fairly deep. Nor could the reason be found in a greater adhesion of seeds and mercury by the secretion of certain substances. For often mercury

<sup>1)</sup> Botanische Untersuchungen von DR. ALBERT WIGAND, Braunschweig 1854 pp. 131—166.

<sup>2)</sup> Idem p. 136.

<sup>3)</sup> Idem p. 137.

<sup>4)</sup> 12 Linien = 1 Zoll = 27,075 mm.

stuck to the radicles, to be sure, but only to old, dying, not to fresh and growing roots.

WIGAND gave no explanation. To him it seemed to be "ein bis jetzt ungelöstes mechanisches Paradoxon, nicht minder als Münchhausen, der sich und sein Pferd an seinem eigenen Zopfe aus dem Sumpfe zieht" <sup>1)</sup>.

But he entirely confused the force with which the root penetrated and the cause which prevents the seedling from capsizing in the mercury. For he thought the penetration of germroots in a solid soil quite as mysterious, although here there was no question of upward pressure.

No attention has later been paid to these observations; not even by those who quoted various other points from this chapter of WIGAND. It was considered sufficient to refer to the refutation by DURAND and DUTROCHET in 1845.

So HOFMEISTER wrote in 1860 <sup>2)</sup>: "PINOT und PAYER sind bereits 1845 durch DURAND und DUTROCHET so gründlich widerlegt, die Ursachen der Täuschungen jener sind so vollständig aufgedeckt worden, dass die ausführliche Mittheilung von mir selbst über diesen Gegenstand angestellter Beobachtungen kaum noch nöthig ist" <sup>3)</sup>. HOFMEISTER obtained the same result as DURAND and DUTROCHET: penetration by weight or because the seedling stuck to the mercury by dissolved matter.

SACHS wrote in 1865: "Die an sich schon unglaublich klingenden Angaben PINOT's und PAYER's über das tiefe Eindringen der Wurzeln in Quecksilber, wurden schon von DURAND und DUTROCHET widerlegt" <sup>4)</sup>.

In 1867 HOFMEISTER wrote that the penetration of growing roots into mercury was caused by stretching of the hypocotyl, "wie bereits DURAND und DUTROCHET erschöpfend gezeigt haben" <sup>5)</sup>.

Experiments on germination upon mercury now became very frequent in the following years in order to combat HOFMEISTER's theory of positive geotropism. This latter namely, like KNIGHT's theory, was based on the supposition that the apex of the root was of a plastic nature and therefore the penetration of the roots into

<sup>1)</sup> l. c. p. 140.

<sup>2)</sup> W. HOFMEISTER, Ueber die durch die Schwerkraft bestimmten Richtungen von Pflanzentheilen, in Berichte über die Verhandlungen der kön. Sächs. Ges. der Wiss. zu Leipzig, Mathematisch-Physische Classe, XIIIter Band 1860, pag. 175—213. The same article in PRINGSHEIM's Jahrbücher für wiss. Botanik III 1863 pag. 77—114.

<sup>3)</sup> l. c. p. 203 resp. p. 105.

<sup>4)</sup> J. SACHS. Handbuch der Experimental-Physiologie der Pflanzen, 1865, pag. 104.

<sup>5)</sup> W. HOFMEISTER. Die Lehre von der Pflanzenzelle, 1867, pag. 283 Anm. 4.

mercury was no welcome fact to these theories. In this way arose the fierce controversy between HOFMEISTER and FRANK <sup>1)</sup>, concerning which we also mention the papers by N. J. C. MÜLLER <sup>2)</sup>, N. SPESCHNEFF <sup>3)</sup>, TH. CIESIELKI <sup>4)</sup>, SACHS <sup>5)</sup>, SAPOSHNIKOW <sup>6)</sup>, and WACHTEL <sup>7)</sup>. FRANK, like WIGAND, derived from DE CANDOLLE <sup>8)</sup> the erroneous idea that PINOT fixed his seeds <sup>9)</sup>, and for the rest entirely embraced the views of DURAND and DETROCHET <sup>10)</sup>. To the loose lying seeds none of them paid attention nor is anything found about them in later text- or handbooks.

In 1899 Dr. A. SCHÖBER gave a historical synopsis of the various hypotheses on geotropism in which he also deals with the experiments on germination upon mercury <sup>11)</sup>. He does not deal with loose seeds in it however.

### *Explanation of the phenomenon.*

The penetration of the roots of entirely freely floating seeds into mercury has been stated by few investigators only. From the preceding historical synopsis it would appear that this was done only by PINOT and WIGAND.

MULDER, GOEPPERT and PAYER gave support to the seed, by putting the roots through holes in a slice of cork (MULDER and PAYER), in a wooden cross (GOEPPERT), or by placing the seeds in or on a plug of cottonwool (PAYER). Hereby the frictional resistance against upward movements was increased and also the circumstances at the surface of mercury and water were modified, so that the seeds were less easily lifted out by upward pressure.

So I repeated the experiments as PINOT and WIGAND had made them. Although WIGAND gives no dimensions, yet one can see from his description that he did not use such small troughs of mercury

1) Bot. Ztg. 1868 and 1869.

2) Bot. Ztg. 1869, 1870 and 1871.

3) Bot. Ztg. 1870.

4) CONN'S Beiträge zur Biologie der Pflanzen I, 2 1872.

5) Arb. des bot. Inst. in Würzburg I, 3 1873.

6) Report in Bot. Jahresbericht XV, 1 1887; less extensive in Bot. Centralblatt Band 33, 1888.

7) Bot. Centralblatt Band 63, 1895.

8) Physiologie végétale II, 1832, pag. 82.

9) Beiträge zur Pflanzenphysiologie, Leipzig 1868, pag. 5.

1) Idem pag. 22.

11) Die Anschauungen über den Geotropismus der Pflanzen seit KNIGHT. Hamburg 1899. pp. 9 and 18.

as PIXON who used them only about one centimetre broad. So I took first rectangular glass troughs of 4 cm. breadth and crystallising dishes of 10 cm. diameter which were filled with mercury about two centimetres deep.

On the dry mercury I had to pour a fairly large quantity of water before this would spread over the whole surface; by means of a pipette so much was drawn off that only a very thin layer remained. In this water the soaked or dry seeds were put. The seeds had to emerge for a great part above the layer of water; if this latter was too thick they rotted and grew mouldy, especially if the temperature was somewhat high, as in a hothouse. The dishes were covered with glass or placed under a bell-jar in order to prevent strong evaporation. Distilled water was used by preference.

The seeds used were: pea (*Pisum sativum*), garden-ress (*Lepidium sativum*), wheat (*Triticum vulgare*), buckwheat (*Polygonum Fagopyrum*) and *Lathyrus odoratus*. The garden-ress grew quickest, so that I could make a number of experiments in succession in a short time with it.

Most roots crept over the surface of the mercury or only penetrated into it with their extreme tip. Sometimes however a radicle had advanced to a fairly considerable depth. Thus on February 19, 1900, the radicle of a seed of garden-ress of two days was 7 mm. long, of which 3 mm. were in the mercury. On March 17, 1900, several radicles of garden-ress had, after three days, advanced 4 to 6 mm. perpendicularly into the mercury, of a pea the radicle was 5 mm. in the mercury. On March 23, 1900, after three days, again a few radicles of garden-ress were 5 mm. in the mercury. The radicles that had found their way into it had for the greater part had a downward direction immediately at their germination, so that only a short piece protruded above the mercury. Sometimes however roots of garden-ress, after having grown laterally about one centimetre, had still pierced the mercury 4 mm. with their apex.

With wheat the three secondary roots crept over the mercury, an apex seldom penetrated any length. Radicles of buckwheat I did not see penetrating. *Lathyrus* sometimes 5 to 7 mm.

On further growth the plantlets that had pierced the mercury were upset and were lifted out of the liquid as was the case with the great majority of seedlings at the very beginning. Hence the experiments were soon finished. So the circumstance that the roots turned black and died later and that the seeds rotted and grew mouldy, gave little trouble. The mercury however had to be perfectly pure, since otherwise the radicles stopped growing too soon

and turned brown. The purification took place with dilute nitric acid.

In these experiments some roots had so far grown down that weight alone could not explain this. My radicles did not go down so deep as those of WIGAND however. Now it soon became clear in what respect the plantlets that had grown into the mercury were distinguished from those which had not. They were not quite free, namely, but lay against another seed; round and between both seeds the water had risen through capillarity and gave some support to the seed by the tension of its concave surface. The molecular forces of the water thus opposed the upward pressure of the mercury.

DURAND calculated the force with which the mercury forces seedlings of *Lathyrus odoratus* upwards. For a cylindrical radicle of  $\frac{3}{4}$  mm. diameter this force amounted per mm. length to  $\pi \left(\frac{3}{8}\right)^2 \times 13,6 = 6$  milligrammes; for a length of 20 mm. this is 120 milligrammes.

The volume of the radicles can be approximately determined from the length and the thickness in various places; or by weighing the cut off radicles. (The specific gravity is about one).

The tapering of the roots towards the top makes the determination of the volume from measurements of thicknesses rather inaccurate. For approximate values the two methods supplement each other sufficiently, however.

For radicles of *Lathyrus* of 5 to 7 mm. length I found volumes of 5 to 8 mm<sup>3</sup>.; the upward pressure of the mercury is then 68 to 109 mg. The *Lathyrus* plantlets weighed about 200 mg.

Roots of garden-cress of 5 to 9 mm. had volumes of 1 to 2 mm<sup>3</sup>.; the upward pressure is then 14 to 27 mg. The cress plantlets weighed, before the seedcoat had fallen off, about 17 mg., after the falling off, 8 mg. <sup>1)</sup>

The weights of the plantlets are considerably diminished, however, by their lying in the water with parts that are much more voluminous than the radicle. When the upward pressure of the layer of water has been subtracted, the weight that must be compared to the upward pressure of the mercury remains. In the case of *Lathyrus* this weight will still be in excess, but with garden-cress there is a greater or smaller deficiency. For the greater depths of PINOT and WIGAND this deficiency becomes greater still, but its amount remains small and can easily be compensated by the molecular forces of the water. If the seedling be raised through a very small distance, the surface of the water that has been raised against the seed by capillarity,

<sup>1)</sup> The cast off seedcoat alone weighs about 16 mg., evidently because it is filled with water, retained by capillarity.

must be extended along the whole margin. The capillary constant of water is 8,8, hence for each mm. of the circumference of the raised water a force of 8,8 mg. is necessary.

This circumference measures with the swollen seed of garden-cress 14 mm., with *Lathyrus* about 29 mm., so that a force of more than 100 mg. is available for compensating differences of upward pressure and weight.

Therefore it is necessary however that the seed or plantlet cannot capsize too easily. The capsizing is a rotation round a horizontal axis by which the water-surface need not be increased. The vertical component of the surface-tension is consequently of no effect to prevent the plantlet from being upset and hence being lifted out. This rotation is rendered more difficult by water, rising by capillarity between two seedlings that lie close together, or between the glass and the seedling, because this water has a greater horizontal surface which must be increased during the capsizing. Hence it is against the glass wall that the roots penetrate most frequently, in which case also the friction between wall and root facilitates the penetration by the unilateral horizontal pressure of the mercury.

The thinner the layer of water, the closer the centres of surface-tension and upward pressure lie together and the shorter is also the lever-arm with which a lateral component of the hydrostatic pressure acts on a somewhat slanting radicle in order to upset the plantlet. With a seed in an entirely free position, penetration will be possible but in the most favourable case only an unstable equilibrium will exist. The penetration of freely placed seeds will consequently be generally absent, not because the upward pressure soon exceeds the weight of the little plant, but because the plant is overturned by rotation.

PINOT immediately obtained such a good result because his mercury-troughs were so small, only one centimetre broad. So I also repeated the experiments in this way. Of a glass tube of one cm. diameter bits were cut off and closed at the bottom with a cork. These troughs were filled with mercury and in each a soaked seed of *Lathyrus* or garden-cress was put with as little water as possible. The water that was raised by capillarity now stuck the seed against the glass wall and the root penetrated more easily because it was less easily upset. When I placed the seeds with the radicle turned towards the centre of the trough, it grew down into the mercury itself, not between the glass wall and the mercury.

PINOT used still another and effective means to prevent capsizing and at the same time to eliminate the weight of the seed, viz. by the experiment with the silver needle, described above. I repeated

this experiment in the following manner, see fig. 1. Of thin sheet-aluminium a flat balance-beam was made,  $6\frac{1}{2}$  cm. long, resting with a brass cap on a steel point. On one end a Lathyrus seed was stuck, to the other a small bit of paraffin was melted, balancing the seed. Exactly under the seed a small trough of mercury was placed with very little water on the mercury. By another small vessel, filled with water, and by a little bell-jar over the whole arrangement, the air was kept moist. The root after a few days grew down 7 mm. into the mercury, without the balance being lifted. By adding to it and by melting away from it, the small bit of paraffin was occasionally brought into equilibrium with the growing seedling, after the latter had been dried with filtering paper. The upward pressure of the mercury which amounted to more than 100 mg., was now balanced by the surface-tension of the water, raised by capillarity. It might even have been a great deal more, for on the other arm of the balance I could still place about 100 mg. in addition to the bit of paraffin before the plantlet was lifted out of the mercury.

We can now explain why various investigators could give such totally contradictory reports.

In the first place we may trust PIXOT's results (1829). The description of his experiments gives the impression that he observed accurately.

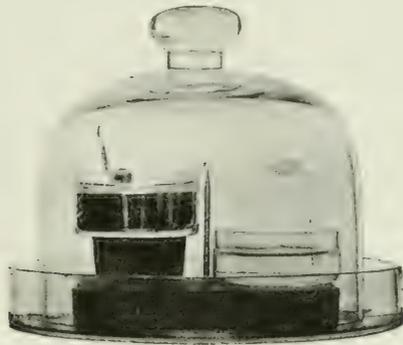
DUTROCHET (1829) did not repeat the experiments with the perseverance which is necessary to obtain a good result.

The experiments of MULDER (1829) were too coarse and valueless for PIXOT's problem. Of GOEPPERT (1831) the same may be said.

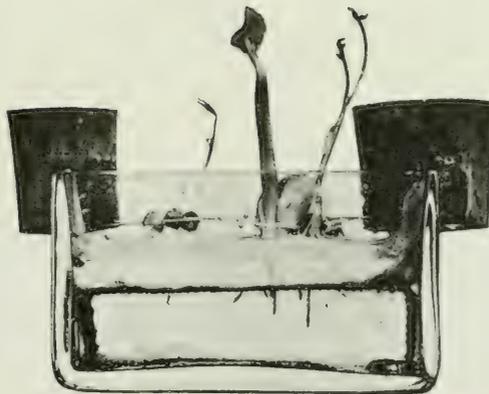
PAYER (1844) used a slice of cork or a plug of cottonwool on a thick layer of water, so that later writers wrongly always mention PIXOT and PAYER together. His experiment, described above, with a layer of mercury above a layer of water, is ingenious. I repeated it, using lacquered iron-gauze instead of platinum-gauze. The roots of seeds of Lathyrus and Phaseolus, stuck on pins in corks, grew very finely through the mercury into the water; see fig. 2. The mercury is indistinct in the figure because of the patch of muslin which lies on the gauze. It was namely pushed downwards in the glass trough in order to show the seeds stuck on the pins.

PAYER stated that the roots did not penetrate again into the mercury once they had been taken out of it. PIXOT and WIGAND asserted the contrary. This can easily be explained. The latter left the seeds free indeed and the surface-tension acted as before when the plant was replaced in the mercury in its former position. PAYER's seedlings, on the other hand, were fixed; they penetrated into the mercury

PH. VAN HARREVELD. „On the penetration into mercury of the roots of freely floating germinating seeds.”



*Fig. 1.*



*Fig. 2.*



to a far greater depth and when they had been taken out of it, they did not so easily regain their former support.

DURAND (1845) gave the explanation which a large, old seedling on mercury suggested to him. It had stayed so long on it, that an adhesive layer had been formed on the mercury of sufficient thickness to fasten the plant to some extent. That therefore all seedlings whose roots penetrate into mercury, should stick to it by such a layer is not true. The penetration takes place after a short time when the mercury is still bright.

DUTROCHET (1845) accepted DURAND's explanation and made experiments on the formation of the sticky layer. But he did not put to himself the question whether in all the observed cases such a "plaster" had been present.

WIGAND (1854) has undoubtedly obtained PIXOT's results. In his discussion however he confused and complicated the question as MULDER had done. For this reason later investigators did not bestow much attention to the paradox which he had so clearly pronounced. Where he speaks of penetration into dry mercury, this must certainly not be taken literally; the soaked seeds retain a layer of water.

HOFMEISTER (1860) studied the penetration of roots in relation with his theory of the plastic apex. He did not obtain the result of PIXOT and WIGAND and accepted DURAND's explanation which also DUTROCHET had accepted.

Later investigators all followed HOFMEISTER's opinion.

**Mathematics.** — "*The harmonic curves belonging to a given plane cubic curve.*" By Prof. JAN DE VRIES.

1. The "harmonic" curve of a given point  $P$  with respect to a given plane cubic curve  $k^3$  is the locus of the point  $H$  separated harmonically from  $P$  by two of the points of intersection  $A_1, A_2, A_3$  of  $k^3$  and  $PH^1$ ). We shall determine the equation of the harmonic curve  $h^3$  when  $k^3$  is indicated by the equation

$$a^3x \equiv b^3x \equiv (a_1x_1 + a_2x_2 + a_3x_3)^{(3)} = 0,$$

and  $P$  by the coordinates  $(y_1, y_2, y_3)$ .

<sup>1</sup>) This curve appears in STEINER's treatise: "Ueber solche algebraische Curven, welche einen Mittelpunkt haben, . . ." (J. of Crellé, XLVII), and is there more generally specified as a curve of order  $n$ . Stereometrically it has been determined by Dr. H. DE VRIES in his dissertation: "Over de restdoorsnede van twee volgens eene vlakke kromme perspectivische kegels, en over satellietkrommen", Amsterdam 1901, p. 6 and 88.

To the points of intersection of  $h^3$  and  $h^3$  belong the points of contact of the six tangents from  $P$  to  $h^3$ . If  $A_1$  is one of the remaining three points of intersection, then  $A_2$  and  $A_3$  are harmonically separated by  $A_1$  and  $P$ , that is  $P$  lies on the polar conic of  $A_1$ ; from this follows however that  $A_1$  lies on the polar line of  $P$ . So the curve  $h^3$  passes through the points of intersection of  $h^3$  with both the polar conic  $p^2$  and the polar line  $p^1$  of  $P$ . Its equation is therefore of the form  $\mu a^3 x + a_y a^2_x b^2_y b_x = 0$ . If point  $X$  belongs to the harmonic curve of point  $Y$ , it is evident that  $Y$  lies on the harmonic curve of  $X$ ; so our equation must be symmetric with regard to the variables  $x_i$  and  $y_i$ ; that is, it has the form

$$a^3_x b^3_y + \lambda a^2_x a_y b_x b^2_y = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

To determine  $\lambda$  we suppose  $P$  to be lying on  $x_3=0$  and we then consider the points of  $h^3$  which are lying on  $x_3=0$ . If we represent the linear factors of the binary form  $a^3 x \equiv b^3 x \equiv (a_1 x_1 + a_2 x_2)^{(3)}$  by  $p_x, q_x$  and  $r_x$ , then the points  $H_1, H_2, H_3$  are indicated by the equation

$$h^3_x \equiv (p_x q_y + p_y q_x) (p_x r_y + p_y r_x) (q_x r_y + q_y r_x) = 0,$$

or by

$$h^3_x \equiv \sum_6 p^2_x q_x q_y r^2_y + 2 p_x p_y q_x q_y r_x r_y = 0 \quad . \quad . \quad . \quad . \quad (2)$$

We now have

$$3 a^2_x a_y \equiv p_x q_x r_y + p_x q_y r_x + p_y q_x r_x,$$

$$3 b_x b^2_y \equiv p_x q_y r_y + p_y q_x r_y + p_y q_y r_x,$$

and as we moreover have

$$p_y q_y r_y \equiv b^3_y,$$

we find out of (2)

$$h^3_x \equiv 9 a^2_x a_y b_x b^2_y - a^3_x b^3_y = 0 \quad . \quad . \quad . \quad . \quad (3)$$

This equation also represents the harmonic curve, if we but again regard  $a^2_x$  as the symbol for  $(a_1 x_1 + a_2 x_2 + a_3 x_3)^{(3)}$ .

2. The polar conic of  $P$  with regard to the curve  $h^3_i$  represented by (1) has as equation

$$3 a^2_x a_y b^3_y + \lambda (2 a_x a^2_y b_x b^2_y + a^2_x a_y b^3_y) = 0,$$

or, if we put

$$a^2_x a_y \equiv K \quad \text{and} \quad a_x a^2_y \equiv L,$$

we find

$$(3 + \lambda) b^3_y K + 2 \lambda L = 0 \quad . \quad . \quad . \quad . \quad (4)$$

It is evident from this that the polar conics of  $P$  with respect to the curves of the pencil determined by  $h^3$  and  $h^3$  touch each other

in their points of intersection with the polar line  $p^1$ , therefore the polar line of  $P$  with respect to all the curves  $k^{\lambda}$  of this pencil.

For the curve  $k^{\lambda}$  passing through  $P$  ensues from this that it must have a node in  $P$ .

Evidently the equation of this curve is

$$a^3_x b^3_y - a^2_x a_y b_x b^2_y = 0, \quad . \quad . \quad . \quad . \quad (5)$$

whilst its polar conic is indicated by

$$a^2_x a_y b^3_y - a_x a^2_y b_x b^2_y = 0,$$

or by

$$b^3_y K - L^2 = 0,$$

from which is evident that it is composed of the tangents through  $P$  to the polar conic  $P$  with respect to  $k^{\lambda}$ .

For  $\lambda = -3$  we find a  $k^{\lambda}$  with the polar conic  $L^2 = 0$ . So it possesses three inflectional tangents meeting in  $P$ .

3. The satellite conic of  $P$  with respect to  $k^{\lambda}$  (that is the conic through the points where  $k^{\lambda}$  is intersected by the tangents drawn out of  $P$ ) has for equation <sup>1)</sup>

$$4 a^2_x a_y b^3_y - 3 a_x a^2_y b_x b^2_y = 0, \quad . \quad . \quad . \quad . \quad (6)$$

or

$$4 b^3_y K - 3 L^2 = 0. \quad . \quad . \quad . \quad . \quad (7)$$

To determine the satellite conic for the curve  $k^{\lambda}$  we put

$$l^{\lambda}_x \equiv a^3_x b^3_y + \lambda a^2_x a_y b_x b^2_y.$$

Then we find

$$3 l^2_x l_y = (\lambda + 3) a^2_x a_y b^3_y + 2 \lambda a_x a^2_y b_x b^2_y;$$

$$6 l_x l^2_y = 2 (\lambda + 3) a_x a^2_y b^3_y + 2 \lambda (a^3_y b_x b^2_y + a_x a^2_y b^3_y),$$

or

$$l_x l^2_y = (\lambda + 1) a_x a^2_y b^3_y;$$

$$l^3_y = (\lambda + 1) a^3_y b^3_y.$$

So according to (6) the equation of the satellite of  $k^{\lambda}$  is

$$4[(\lambda + 3) a^2_x a_y b^3_y + 2 \lambda a_x a^2_y b_x b^2_y] (\lambda + 1) c^3_y d^3_y - 9 (\lambda + 1)^2 a_x a^2_y b^3_y c^2_y d^2_y = 0,$$

or as  $a, b, c$  and  $d$  are equivalent symbols,

$$(4 \lambda + 12) a^2_x a_y b^3_y - (\lambda + 9) a_x a^2_y b_x b^2_y = 0,$$

or

$$(4 \lambda + 12) b^3_y K - (\lambda + 9) L^2 = 0. \quad . \quad . \quad . \quad . \quad (8)$$

From this ensues that the satellite conics and the polar conics of  $P$  with respect to the curves  $k^{\lambda}$  belong to the same pencil. If we represent this by the equation

<sup>1)</sup> The deduction of this equation is found in SALMON "Higher plane curves". A stereometrical treatment of the satellite curves is found in the above-mentioned dissertation of Dr. H. DE VRIES, p. 18, 19 etc.



it is evident that the harmonic curves of  $P$  with respect to the curves of the cubic pencil also form a system with index *two*.

For  $k^3$  passing through  $P$  the curve  $h^3$  breaks up into the system of the polar conic and the polar line of  $P$  with respect to that curve which touch each other in  $P$ .

As  $k^3$  and  $h^3$  have in common the tangents out of  $P$ , being thus of the same class, the harmonic curve has only then a node when this is the case with the original curve.

5. If with respect to a given  $k^3$  we determine on each right line through  $P$  the points  $B_1, B_2, B_3$  in such a way that  $B_i$  is harmonically separated by  $A_i$  from  $A_j$  and  $A_k$ , we get as locus of the points  $B$  a curve of order *sive*,  $h^6$ , with a threefold point in  $P$ . For, if  $B_1$  coincides with  $P$ , then  $A_1$  is one of the points of intersection of  $k^3$  with the polar line of  $P$  and the reverse (see § 1).

As the points  $B$  correspond one by one to the points  $A$ , the curve  $h^6$  is of the same genus as  $k^3$ , so it has still 6 double points or cusps. This last is excluded because in that case not a single tangent could be drawn from  $P$  to  $h^6$ , whilst it is clear that the tangents out of  $P$  to  $k^3$  also touch  $h^6$ .

From the definition of  $h^6$  follows immediately that this curve can meet the curve  $k^3$  only in the points of contact  $R$  of the above mentioned six tangents: so in each point  $R$  they have three points in common. The right line  $PR$  having in  $R$  two points in common with  $k^3$ , but three points with  $h^6$ ,  $R$  must be one of the six nodes of  $h^6$  and  $PR$  one of the tangents in that node.

**Chemistry.** — "*Preparation of cyclohexanol.*" By Prof. A. F. HOLLEMAN.

The preparation of ketohexamethylene in somewhat large quantities is one of the most lengthy operations, whatever known process may be used.

Since, by means of the addition of hydrogen to benzene, by the process of SABATIER and SENDERENS, hexa-hydrobenzene has become a readily accessible substance, it was thought advisable to use this as a starting point for the preparation of the said ketone by first converting it into monochlorohexamethylene, converting this in the usual manner into the corresponding alcohol and then oxidising this to ketone by the process indicated by BAEYER. MR. VAN DER LAAN has tried, in my laboratory to realise this.

The method, however, appeared impracticable as the chlorocyclohexane was not readily converted into the alcohol. MARKOWNIKOFF has tried to attain this by using alcoholic potash; we have tried it by shaking the said chloro-compound for several days and at different temperatures with silver oxide and water + alcohol, but a transformation worthy of the name was not controlled.

The chlorination of cyclohexane in quantities of 80—100 grams to the monochloro-compound was moreover a disagreeable and slow operation. The most satisfactory results were obtained by MARKOWNIKOFF's first method (A. 301, 184) by pouring the hydrocarbon on to water in a Drechsel flask and then passing chlorine into the water at 30—40°. The influence of light is very pronounced in this case. Direct sunlight causes explosion. If chlorine is passed through the hydrocarbon exposed to faint light it dissolves with a yellow colour. If now this solution is exposed to sunlight a violent evolution of hydrogen chloride takes place; in strong light this is accompanied by luminous phenomena.

Mr. VAN DER LAAN, however, succeeded in readily preparing keto-hexamethylene by another process. It appeared that phenol and hydrogen combine to hexahydrophenol by the method of SABATIER and SENDERENS and that the cyclohexanol obtained could then be oxidised to the corresponding ketone:



For the preparation of cyclohexanol  $\text{C}_6\text{H}_{11}\text{OH}$  a combustion tube was quite filled with nickeloxide which was then reduced by means of pure hydrogen. By means of an asbestos stopper, one end of the tube was connected with a wash-bottle containing phenol; this was placed in an airbath heated to 160—170°. The tube was placed in a combustion furnace in an iron gutter lined with asbestos. The bulbs of two thermometers were also placed in the gutter and the flames were so regulated that they showed 140—160°. By means of another asbestos stopper, the other end of the tube was connected with an adapter leading into a flask closed with a doubly-perforated cork. Through the second hole was passed a gas exit tube by means of which the absorption could be controlled.

The current of pure and dry hydrogen which was passed into the wash-bottle containing the phenol charged itself with vapour which in the presence of an excess of hydrogen was exposed to the catalytic action of the nickel.

In the receiver a liquid consisting of two layers collected, the bottom layer being water.

The top layer was submitted to distillation. From 85°—110° a liquid

distilled, which separated into two layers one of which consisted of water whilst the other had a bitter peppermint-like odour. From  $110^{\circ}$  the temperature rapidly rose to  $160^{\circ}$  and from  $160-180^{\circ}$  a considerable fraction passed over. What distilled above  $180^{\circ}$  was mainly unchanged phenol, which was again subjected to treatment with hydrogen. To remove any phenol, the fraction  $160-180^{\circ}$  was washed a few times with dilute soda-lye, the alkaline washings were shaken with ether to recover any dissolved cyclohexanol, the ether was evaporated and the residue united with the main liquid. After a few more distillations a liquid was obtained, perfectly clear and of a thick consistency, boiling at  $160-161^{\circ}$ , the b.p. of cyclohexanol being recorded as  $160^{\circ}.3$ . A combustion gave the following result. 0.1740 gm. gave 0.4610 gm.  $\text{CO}_2$  and 0.2017 gm.  $\text{H}_2\text{O}$ ; found:

C 72.2 H 12.8

calculated for  $\text{C}_6\text{H}_{12}\text{O}$ : C 72.0 H 12.0

By oxidation with BECKMANN'S chromic acid mixture (1 mol.  $\text{K}_2\text{Cr}_2\text{O}_7 + 2\frac{1}{2}$  mol  $\text{H}_2\text{SO}_4$  in 300 grms. of water) of which 135 grams were used for 10 grams of hexanol and operating at a low temperature, hexanol gives a fair yield of ketohexamethylene.

MR. VAN DER LAAN has not determined the exact amount of cyclohexanol obtainable from phenol but this is certain that the yield is quite satisfactory. If four tubes with nickelpowder are heated at the same time 1 kilo of hexanol may be easily prepared within 7 or 10 days.

As a result of this investigation some substances which were only accessible with the greatest difficulty, have now become easy of preparation. First of all cyclohexanol and ketohexamethylene. The latter may be nearly quantitatively oxidised to adipic acid and as its calcium salt gives a fair yield of ketopentamethylene when submitted to dry distillation, these two latter substances are no longer to be regarded as chemical curiosities.

*Groningen, Lab. Univ. September 1903.*

**Vegetable Physiology.** — *“Investigations of some xanthin derivatives in connection with the internal mutation of plants”*. By Dr. TH. WEEVERS and MRS. C. J. WEEVERS — DE GRAAFF. (Communicated by Prof. C. A. LOBRY DE BRUIN).

The investigations of CLAUTRIAU<sup>1)</sup> and of SUZUKI<sup>2)</sup> as to the function of caffeine have shown that this substance must probably be regarded as a decomposition (“Abbau”) product of albumenoids.

<sup>1)</sup> G. CLAUTRIAU. *Nature et Signification des Alcaloides végétaux*, Bruxelles 1900.

<sup>2)</sup> SUZUKI. *Bull. Coll. Agric. Tokyo Imp. Univ.* Vol. 4. 1901. pag. 289.

These investigations, however, did not clearly show that the caffeine when once formed again took part in the internal mutation processes; they rather pointed to a preservation of this substance as such and in such cases where it was shown that the quantity of caffeine had decreased, this might have, possibly, been due to migration.

We, therefore thought it desirable to subject plants containing xanthine derivatives to a renewed investigation, to examine as many species as possible and particularly to study the question whether these xanthine derivatives are an intermediary or a final product of the internal mutation. *Coffea* and *Thea* species were the only plants investigated up to the present so we also included in our research *Kola acuminata* Horsf. et Benn. and *Theobroma Cacao* both of which contain caffeine as well as theobromine. A stay at the Botanical Gardens at Buitenzorg (Java) afforded us ample opportunity <sup>1)</sup>.

At Buitenzorg many physiological experiments were made and material collected for quantitative determinations, the results of which will be published later on; qualitative and microchemical tests were also made and of these a short description will be given below.

First of all a few words as to the methods employed for the detection of the xanthine derivatives in the various parts.

BEHRENS's method was used for plants containing caffeine only. The parts were triturated in a mortar with quick lime and extracted with 96% alcohol. A few drops of the alcoholic solution were then evaporated to dryness and the residue sublimed. The sublimate after breathing on it then showed crystals of hydrated caffeine.

In the case of plants containing both caffeine and theobromine the parts were boiled with water slightly acidified with acetic acid. The aqueous extract was filtered and precipitated with lead acetate; the filtrate after being neutralised with sodium carbonate was then evaporated to dryness. Up to this stage the method proposed by BEHRENS had been again used but the dry mass was not now heated in order to sublime the xanthine derivatives but was extracted with a little chloroform. Both xanthine derivatives passed into this solvent and on evaporating the same they were left behind as well defined crystals; sometimes the residue had to be first sublimed.

Both methods are very delicate; traces of either caffeine or theobromine may be detected.

The investigation extended over the following plants: *Coffea arabica* L., *C. liberica* Bull., *C. stenophylla* G. Don., *Thea assamica*

<sup>1)</sup> *Paullinia sorbilis* Mart. and *Ilex paraguariensis* St. Hilaire could not be investigated but we hope to do so on some future occasion.

Griff., *T. sinensis* Sims., *Kola acuminata* Horsf. et Benn. and *Theobroma Cacao* L.<sup>1)</sup>.

a. *Roots:*

In *Thea* sp.<sup>2)</sup> *Coffea* sp. and *Theobroma* neither the roots of the full grown plants, nor those of the seedlings showed traces of caffeine or theobromine. In *Kola acuminata* the roots of the full grown specimens did not show any either; those of the seedlings, however, contained theobromine but no caffeine.

b. *Stems:*

1. Extending young shoots contained:

caffeine in *Thea* sp. and *Coffea* sp.

caffeine and theobromine in *Kola acuminata*.

theobromine no caffeine in *Theobroma Cacao*.

2. One year old branches contained:

caffeine in *T. assamica*, *T. sinensis*, *Coffea liberica*, *C. arabica*; no caffeine or theobromine in *Coffea stenophylla*, *Theobroma Cacao*, *Kola acuminata*.

3. Two years old branches contained:

caffeine in *T. assamica*, *T. sinensis*, *Coffea arabica*, none in any of the others<sup>3)</sup>.

In branches, these xanthine derivatives are always found in the bark and not in the wood, at least if the branches are old enough to render possible a neat separation of the two.

c. *Leaves:*

1. young leaves of *Thea* sp. and *Coffea* sp. contained caffeine, those of *Theobroma Cacao* and *Kola acuminata* theobromine and caffeine.

2. Full grown leaves of *Thea* sp., *Coffea arabica* and *Coffea liberica* contained caffeine; those of *Theobroma Cacao* traces of theobromine. Those of *Coffea stenophylla* contained no caffeine, those of *Kola acuminata* neither theobromine nor caffeine.

d. *Flowers:*

*Thea assamica*: caffeine in all parts of the flowers, calyx, petals, stamens and pistil.

*Coffea liberica*: caffeine in the pistil only.

*Theobroma Cacao*: theobromine (no caffeine) in the pistil only.

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<sup>1)</sup> *Coffea bengalensis* Roxb. *Camellia japonica* L., *C. Sasangua* Thb. and *C. minahassae* Koorders were also tested but in neither of them any caffeine was found.

<sup>2)</sup> These species are only those mentioned above and not those in note 1.

<sup>3)</sup> The bark of very thick old branches of *Thea assamica* contains caffeine; none is found in that of *Thea sinensis*.

*Kola acuminata*: caffeine and theobromine both in the petals and stamens of the ♂ and in the corolla and pistil of the ♀ flowers<sup>1)</sup>.

e. *Fruits*:

*Thea* sp.: both young and ripe seeds (in husk) contained caffeine (but only in very small quantities).

*Coffea* sp.: much caffeine in the cotyllae and also in the testa and husk.

*Theobroma Cacao*: When the fruit is ripening, theobromine first makes its appearance in the external fruit wall; afterwards a xanthine derivative (caffeine) occurs in the fruit pulp; finally the seeds themselves show the presence of theobromine and caffeine while the theobromine is disappearing from the external fruit wall.

*Kola acuminata*: The fruit wall, fruit pulp and also the seeds contain both xanthine derivatives during the maturation process.

On looking at these facts we first of all observe that the said xanthine derivatives are present in all the young parts of these plants which grow above ground even when they spring from old parts utterly devoid of these substances. For instance, the flowers of *Coffea liberica* sometimes result from old branches, the bark of which is devoid of caffeine and still they contain this substance. In the case of *Theobroma Cacao* the flower branches (and sometimes the young shoots) always spring from old branches utterly devoid of theobromine and with *Kola acuminata* this is still more pronounced; the flowers and young shoots always result from branches in which no theobromine or caffeine can be detected either before or after the budding.

From this it is evident that during the period of development and growth of the young parts of the said plants, caffeine or theobromine is always formed and remains localized in those parts for a longer or shorter period. This fact may be very well reconciled with the theory that these substances may be decomposition products of albumenoids<sup>2)</sup> although, perhaps another explanation may be possible.

At the same time, however, it appears from the above that these xanthine derivatives very often diminish in quantity during the growth of the young parts and that they disappear from the full grown ones.

They are found to disappear from the leaves of *Coffea stenophylla*, *Theobroma Cacao* and *Kola acuminata*, from the branches of these species and from those of *Thea sinensis*, *Coffea liberica* and *C. ara-*

1) Flowers of *T. sinensis* and *Coffea arabica* were not at our disposal.

2) How the facts observed with roots may be reconciled with this theory remains as yet unexplained.

bica; one would, therefore, be inclined to think that caffeine and theobromine may again take part in the internal mutation.

Let us, therefore, take the case of a fairly young non-blossoming specimen of *Kola acuminata*.

During the unfolding of the young buds the plant is very rich in caffeine and theobromine; the young leaves and branches, however, retain these substances for a short time only, so that after two months they have completely disappeared. There is then not a single part, young or old which contains any caffeine or theobromine and as no parts have become detached, this fact can only be explained by assuming that these xanthine derivatives have again entered into the internal mutation.

With the *Thea* species the matter appears quite different; the young leaves and also the full grown ones are rich in caffeine and the quantity found in the bark is a mere nothing as compared with that contained in the leaves. Here it would appear as if, with the falling of the leaves, the caffeine as such would be lost; this view, however, is not correct.

On testing tea leaves which had turned yellow and would fall at the merest touch, it appeared that they were quite *caffeine-free* both in the case of *Thea assamica* and *T. sinensis*. The same was noticed with *Coffea liberica* and *Theobroma Cacao* (also in regard to theobromine) that is to say in the case of all species whose full grown leaves still contained xanthine derivatives, with the exception of *Coffea arabica*. During our stay at Buitenzorg it was, however, not possible to obtain leaves which had fallen after having turned yellow in the normal manner. All the leaves had been attacked by *Hemileia vastatrix* which causes a premature turning yellow and falling. It is probably due to this fact that no caffeine-free yellow leaves were met with.

We, therefore, see that these xanthine derivatives disappear from the leaves shortly before they fall, whilst the bark of the older branches bearing these leaves is either free from these substances (and remains so as in the case of *Theobroma Cacao* and *Coffea liberica*) or contains such a trifling quantity thereof that it is as nothing compared with the quantity disappeared from the leaves, as in the case of *Thea* sp.

If we now take into consideration that the leaves of the branches which are quite devoid of young shoots or flowers also show the same behaviour, we can state with certainty that the xanthine derivatives again enter into the internal mutation and are, therefore, at least in this case, an *intermediary* and *not a final* product. This

conclusion may be supported by quantitative determinations, but these are not necessary in order to prove its correctness.

The shrubs of *Thea assamica* of the Agricultural Garden at Tjikeumeuh bear a number of variegated leaves often so discoloured that one side of the midrib is yellow whilst the other side is green.

These two sections which are of course, equally old and exactly similar and which differ only by the absence or presence of chlorophyll, were compared as to their amount of caffeine. The operation was conducted in the manner previously described <sup>1)</sup> for catechol.

Of a small number of leaves a yellow and an equally large green piece was taken, both were triturated separately with quick lime, extracted with the same amount of alcohol and the deposits obtained by sublimation were then compared.

Each time the sublimate obtained from the yellow part of the leaves were found to be much denser; the part free from chlorophyll consequently contains decidedly more caffeine than the one containing chlorophyll; a very significant fact which may enable us to get a better insight into the chemical processes of this plant.

At the end of this preliminary communication we desire to thank Prof. VAN ROMBURGH acting director of the Botanical Gardens at Buitenzorg, for his kind assistance.

**Mathematics.** — “*Rectifying curves.*” By MR. J. VAN DE GRIEND JR. communicated by Prof. J. CARDINAAL.

It is known that every motion of an invariable plane system can be regarded as the rolling of a definite curve of the moving system (the “movable polar curve”) over another definite curve of the immovable plane (the “fixed polar curve”). In the following paper the special case will be treated of this general motion, where the movable polar curve is a right line and the motion therefore consists in the rolling of one of the tangents of the fixed polar curve over that curve.

Here, however, the constant polar curve itself will not be given; according to a stated law (see N<sup>o</sup>. 1) this will have to be deduced from another curve given in the moving plane (its rectifying curve) which takes its place and determines it by means of the rectilinear movable polar curve. The replacement of the fixed polar curve by its rectifying curve will give rise to the advantage that in some cases the rectifying curve will be a much simpler one than the rectified

<sup>1)</sup> Investigations of glucosides in connection with the internal mutation of plants. September 1902,

polar curve itself, which will cause its properties to be easily studied and calculations of surface and length of arc to be executed in an easier way. And it will be possible to trace in what way the considered fixed polar curve can be described by other curves, the rectifying ones of which are likewise given (N<sup>o</sup>. 3,4). Moreover the investigation of these rectifying curves in a certain case (N<sup>o</sup>. 12) leads back to two kinds of spirals, found already by PUISEUX in consequence of their tautochronism for forces proportional to the distance (Journal de Lionville, T. IX), but of which by this theory more could be found about their geometrical properties.

Summing up in the following the chief points of my investigations very concisely I intend, if possible, to revert to them more in detail.

§ 1. *Notion of the rectifying curve; simplest case.*

1. Given in a movable plane an invariable system ( $\Sigma$ ) consisting of a right line  $AB$  (the *axis* fig. 1a) and a curve ( $F$ ). The system moves with the axis  $AB$  as movable polar curve. Let point  $Q$  of this axis be the momentary pole,  $Q'$  the following,  $QP$  and  $Q'P' \perp AB$ . Let the elementary rotation  $d\varepsilon$  round  $Q'$  be taken of such a dimension that the right line  $Q'P'$  coincides after the rotation with  $QP$  regarded as a right line of the immovable plane; let then the rotation around  $Q''$  be taken in such a way that  $Q''P''$  coincides with  $Q'P'$  etc. Then point  $Q$  describes a curve ( $f'$ )(fig. 1b) the locus of the poles in the immovable plane, so the fixed polar curve or the envelope of the axis  $AB$  in the immovable plane.

We call ( $F$ ) the *rectifying curve* of ( $f'$ ); then ( $f'$ ) itself is the *rectified curve* with respect to ( $F$ ).

The lines  $QP$  and  $Q'P'$  being two successive normals of the curve ( $f'$ ) cutting each other in  $P$ , the point  $P$  is the centre of curvature of ( $f'$ ).

If we assume in the system ( $\Sigma$ ) the axis  $AB$  as  $x$ -axis and a right line  $OY$  perpendicular to it as  $y$ -axis, we then immediately see on account of the nature of the generation of the curve:

a. that the abscissae  $x$  of ( $F$ ) are the lengths of arc and the ordinates  $y$  are the radii of curvature of ( $f'$ ), so that the rectifying curve is at the same time the curve representing the radius of curvature  $\rho$  as a function of the arc  $s$ ;

b. that the elementary rotation of the system ( $\Sigma$ ) or the angle of contingency of ( $f'$ ) is  $d\varepsilon = \frac{dx}{y}$ ;

c. that the trajectory of point  $P$  moving along ( $F$ ) in the immo-

vable plane is the evolute of ( $f'$ ) of which the length of arc is found on the ordinate of ( $F$ );

*d.* that the trajectory of an arbitrary fixed point  $C$  of  $AB$  is one of the evolvents of ( $f'$ ) starting from that point of ( $f'$ ), which becomes the pole in the immovable plane when  $Q$  is in  $C$ ;

*e.* that the area of the figure, comprised between the rectified curve ( $f'$ ), its evolute ( $P$ ) and two of its radii of curvature, is half of the area of the figure between ( $F$ ), the axis  $AB$  and the corresponding ordinates.

2. *Right line as rectifying curve.* Let the rectifying curve be the right line  $AB$  (fig. 2) and let the motion have advanced as far as the pole  $Q$ , centre of curvature of ( $f$ )  $P$ . The following motion is an elementary rotation  $d\varepsilon = \angle P'Q'P$  or  $\angle QPQ'$  round  $Q'$ . If we let fall out of  $Q$  and  $Q'$  perpendiculars  $QV$  and  $Q'V'$  on  $AB$ , then at the limit the points  $V$  and  $V'$  lie on the circle, described on  $PQ$  as a diameter. So  $\angle QVQ' = \angle QPQ'$ , consequently also  $\angle VQ'V' = \angle P'Q'P$ , the elementary rotation. Furthermore  $\angle Q'V'A$  being a right angle the system rotation round  $Q'$  causes point  $V'$  to arrive in  $V$  represented as a point of the immovable plane. The same holds good for the following rotations. So the (variable) projection  $V$  of  $Q$  on  $AB$  in the immovable plane is a fixed point. As moreover the angle  $VQA$  (angle of the tangent of the rectified curve with the radius vector out of  $V$ ) remains constant, the rectified curve is a logarithmic spiral with  $V$  for pole.

The trajectory of the pole of the logarithmic spiral in the movable system is the right line  $AB$ . So when a logarithmic spiral rolls over one of its tangents, its pole describes a right line.

The place of the pole in the movable system is found for every moment by projecting the corresponding momentary centre  $Q$  of the motion on the right line ( $F'$ ). The part  $QA$  of the  $x$ -axis corresponds to the arc of the logarithmic spiral, which approaching the pole, winds round it in an infinite number of revolutions; the point  $A$  of the  $x$ -axis is unattainable by this arc;  $QA$  is the limit of the length of arc of  $Q$  measured towards the pole. The shape of the logarithmic spiral depends exclusively upon *one* datum: the angle of the right line ( $F'$ ) with the  $x$ -axis.

As a special case there is the right line parallel to the  $x$ -axis as rectifying curve: the rectified one becomes a circle (logarithmic spiral where the angle between radius vector and tangent is a right one; the pole of the spiral becomes the centre of the circle.)

§ 2. *Movable and variable rectifying curves.*

3. If two curves  $(f)$  and  $(f')$  osculate each other in a point  $Q$  and if the evolute  $(p')$  of the latter is allowed to roll over the evolute  $(p)$  of the former, the curve  $(f)$  which does not move, will be the envelope of the moving curve  $(f')$  described osculatingly by it in all points; the point of contact  $Q$  displacing itself along the moving curve  $(f')$  describes the fixed curve  $(f)$ .

Let us take of  $(f)$  and  $(f')$  the rectifying curves  $(F)$  and  $(F')$  (Fig. 3), then for the first condition (osculating each other in  $Q$ ) the  $x$ -axes of these rectifying curves must coincide and the two rectifying curves must intersect each other in  $P$  perpendicularly over  $Q$ . The following ordinate (radius of curvature of  $(f')$ )  $P'_1Q'_1$  of  $(F')$  is equal to the ordinate (radius of curvature of  $(f)$ )  $P_1Q_1$  of  $(F)$ . To make these rays of curvature coincide a displacement of the system of the rectifying curves  $(F')$  is necessary over a distance  $Q'_1Q_1$ .

So the above-mentioned osculating description of a curve  $(f)$  by another curve  $(f')$  corresponds to the description of its rectifying curve  $(F)$  by the rectifying curve  $(F')$  by means of a parallel displacement of  $(F')$  parallel to the  $x$ -axis; the variable point of intersection  $P$  on  $(F')$  describes the curve  $(F)$ . The amount of the elementary displacement  $Q'_1Q_1 = dx - dx'$  is determined by the difference of the abscis-elements  $dx$  and  $dx'$  which correspond in both curves to the increase of the coinciding ordinate  $y$  to the following ordinate  $y + dy$ .

4. When the rectifying curve  $(F')$  does not intersect the rectifying curve  $(F)$  but touches it, the rectified curve  $(f')$  has the following radius of curvature in common with  $(f)$  which it touches by a contact of the third order (four consecutive points in common). If we allow  $(F)$  to be described envelopingly by the rectifying curve  $(F')$  which then not only changes its position but also its shape according to a definite law, then this corresponds to the description in fourpoint contact of the rectified curve  $(f)$  by the variable and moving rectified curve  $(f')$ .

The evolute of  $(f)$  is described osculatingly by the variable and moving evolute of  $(f')$ ; the evolute of the evolute of  $(f)$  is enveloped by that of  $(f')$  in twopoint contact.

5. In particular an arbitrary rectifying curve can be described intersectingly by a right line of constant direction or tangentially by a right line of variable direction; this is (2) every curve in threepoint contact by a constant logarithmic spiral or in fourpoint contact

by a variable logarithmic spiral. If the right line of the constant direction is parallel to the  $x$ -axis, then the osculating spiral becomes circle of curvature (however not remaining of constant size during the motion). So the osculating description of a curve ( $f$ ) by a variable circle of which the centre generates its evolute, becomes a special case of the osculating description by a constant logarithmic spiral, of which the pole  $W$  (determined according to 2) generates a definite curve to be called an *oblique evolute* of ( $f$ ) (because it is formed by the intersection of the successive right lines forming with the successive tangents of ( $f$ ) a constant oblique angle). By changing the oblique angle we obtain for one and the same curve ( $f$ ) an infinite number of these oblique evolutes. In contrast to this there is only one single trajectory of the pole of the variable logarithmic spiral in four-point contact; the pole  $V$  of this spiral is found in every position of the system by projecting the describing point  $Q$  of ( $f$ ) on the tangent of the rectifying curve in  $P$ . We wish to determine the tangent and the radius of curvature (7, 8) of the oblique evolutes or trajectories of the poles of the logarithmic spirals in threepoint contact and of that of the spiral in fourpoint contact. Some investigations must however precede concerning the motion of the line connecting  $Q$  and  $V$  (6).

6. To determine the point of contact <sup>1)</sup> of the right line  $QV$  (fig. 4) we notice that the motion of this right line as invariable system is determined by the motion of the point  $Q$  following the describing point of ( $f$ ) and having thus a displacement equal to  $dx$  along  $SQ$ , and the condition  $QV \perp SP$ , must remain tangent to ( $F$ ). For the latter it is necessary that the rotation of  $QV$  is equal to that of  $SP$ ; so we have first to determine the motion of  $SP$  (invariable system determined by the motion of  $P$  as the describing point of the evolute of ( $f$ ) (1 c)) and the contact of ( $F$ ). The motion of  $SP$  results from two rotations: the system rotation  $d\varepsilon = \frac{dx}{y}$  round  $Q$  and the rotation  $d\varepsilon'$  of the radius of curvature  $MP$  round the centre of curvature  $M$  of the rectifying curve ( $F$ ), which gives the tangent  $SP$  its following position. So the momentary centre of the resulting motion of  $SP$  lies on  $MQ$ ; moreover  $P$  having in consequence of this resulting motion to cover the element of arc of the evolute of ( $f$ ), that is having to undergo a displacement  $dy \perp AQ$ , the momentary centre must also lie on  $PI \perp PQ$  and is thus the

<sup>1)</sup> Point of intersection of the right line  $QV$  with its following position.

point of intersection  $U$  of  $MQ$  with  $PI$ . The rotation of  $SP$  round this point is  $\frac{QM}{UM}$  times the rotation round  $Q$ , that is  $\frac{QM}{UM} \times d\varepsilon$ .

This same rotation must be performed by the invariable system  $QV$  round its unknown momentary centre  $X$ , whilst  $Q$  is displaced along  $AQ$  covering a distance  $= dx = y d\varepsilon$ . From the latter ensues that the unknown momentary centre  $X$  must lie on  $QP$ , where  $XQ \times \frac{QM}{UM} \times d\varepsilon = y d\varepsilon$ . From this we find

$$\frac{XQ}{y} = \frac{UM}{QM} = \frac{PM}{DM}.$$

Therefore the point of contact  $R$  of  $QV$  is found by drawing  $XR \perp QV$  and as also  $PV \perp QV$ , the above mentioned equation becomes

$$\frac{RQ}{VQ} = \frac{PM}{DM}.$$

So this is the equation which determines the position of the point of contact  $R$  on  $QV$ .

### 7. Trajectory ( $V$ ) of the pole of the logarithmic spiral in four-point contact.

a). *Tangent.* Let us describe a circle ( $N$ ) through  $P$ ,  $V$  and  $Q$  (fig. 4), we can then regard this circle as a similar varying system of which point  $P$  has a motion  $dy \perp SQ$  and point  $Q$  a motion  $dx$  along  $SQ$ . The centre of the velocities of this motion is  $V$ , because  $\angle VPP' = \angle VQQ'$  and  $VP: VQ = dy: dx$ . This centre of the velocities being situated on circle ( $N$ ) itself, it is at the same time one of the points of contact of circle ( $N$ ). Point  $V$  has in general displaced itself along the circle in its second position; the tangents of the two positions in  $V$  differ infinitesimally, so the tangent to the trajectory ( $V$ ) is the tangent  $VV'$  to the circle ( $N$ ) in  $V$ .

b). *Radius of curvature.* To find the centre of curvature of the trajectory ( $V$ ) let us search for the point of intersection of two consecutive normals  $NV$  of this trajectory. For that purpose we shall consider  $\triangle V N Q$ . The vertex  $Q$  is displaced in the direction  $QQ'$ , the vertex  $V$  according to the tangent  $VV'$ , the vertex  $N$ , as a point of the similar system ( $N$ ), in the direction  $NN'$ , if  $\angle V N N' = \angle V Q Q'$ . We can easily convince ourselves that these three directions concur in *one* point. So the triangle moves perspectively; so the points of contact of the sides lie in one right line. The point of contact of  $NQ$  (normal of the curve ( $f'$ )) is  $P$  (centre of curvature of ( $f'$ )); the point of contact of  $QV$  is  $R$  (6). We then

find the point of  $VN$ , in other words the required centre of curvature  $M_v$  of  $(V)$  as the point of intersection of  $NV$  with  $PR$ .

8. *Trajectory (W) of the pole of the constant logarithmic spiral in threepoint contact.*

a). *Tangent.* Let the rectifying curve of the logarithmic spiral be  $S_wP$  (fig. 5), pole  $W$ .

Angle  $PS_wQ$  remaining constant the triangle  $PWQ$  forms during the whole motion a similar varying system. Of this system  $V$ , the pole of the spiral in fourpoint contact (7), is the centre of the velocities, because  $\angle VPP' = \angle VQQ'$  and  $VP: VQ = dy: dx$ . So the vertex  $W$  of  $\triangle PWQ$  moves in such a way that  $\angle VWW' = \angle VPP'$ . As  $P, W, V, Q$  are concyclic it is easy to see that  $WW'$  lies in the production of  $QW$ . So  $QW$  is the tangent to the trajectory  $(W)$ .

b). *Radius of curvature.* To find the centre of curvature of the trajectory  $(W)$  we must find the point of contact of the normal  $PW$  of this trajectory, that is that point of  $PW$  of which the motion is directed according to  $PW$  itself, if we regard this right line again as a right line of the similar varying system  $QWP$ . This point is found by letting down  $VM_w$  out of the centre of velocities  $V$  in such a way that  $\angle VM_wS_w = \angle VPP'$ , or  $\angle VM_wP =$  supplement of  $\angle VPP' = \angle VIP$ . So  $I, M_w, V, P$  lie on a circle and  $\angle IVP$  being a right angle  $\angle IM_wP$  is a right one too. So the desired centre of curvature  $M_w$  is found by producing  $QV \perp S_wP$  till it intersects  $PI$  in  $I$  and by letting down a perpendicular  $IM_w$  out of  $I$  on to  $S_wP$ .

### § 3. Conics on their axes as rectifying curves.

9. As a means for the treatment of the conics as rectifying curves let us first regard the right line  $PN$  (fig. 6), where  $P$  in the system motion of  $(\Sigma)$  describes the evolute of  $(f)$  whilst  $N$  is a fixed point of the  $x$ -axis and let us then determine its point of contact. The right line  $PN$  of which the motion is determined by the motion of  $P$  and  $N$  ( $P$  describes the evolute,  $N$  one of the evolvents of  $(f)$  (1)), can be regarded as a similar system; point  $P$  has a motion  $= dy \perp AN$ ; point  $N$ , as a consequence of the system rotation  $= d\epsilon$  about  $Q$ , a motion  $= QN \times d\epsilon$  likewise  $\perp AN$ . So the point of contact  $T$  in question lies on  $PN$  in such a way that

$$\frac{TP}{TN} = \frac{dy}{QN \times d\epsilon}$$

Now  $d\varepsilon$  is equal to  $\frac{dx}{y}$  (1), so  $\frac{TP}{TN} = \frac{y}{QN} \frac{dy}{dx}$ ;  $y \frac{dy}{dx} = PI$ , if we produce  $QV$  tangent  $SP$  as far as the intersection  $I$  with  $PI // x$ -axis. So

$$\frac{TP}{TN} = \frac{PI}{QN}$$

That is: the point of contact  $T$  in question is the point where  $PN$  is intersected by  $QV$ .

10. *Ellipse on one of its axes as rectifying curve.* If we take for the constant point  $N$  of the  $x$ -axis (9) the centre  $O$  of the ellipse (fig. 7), then the displacements of  $O$  and  $P$  are respectively  $QO$ .  $d\varepsilon = x d\varepsilon = x \frac{-dx}{y}$  and  $dy$ ; the quotient  $\frac{-x dx}{y dy}$  is according to the central equation of the ellipse constant  $= \frac{a^2}{b^2}$ . So the point of contact of the right line  $OP$  remains during the whole motion a fixed point; this point of contact is the point  $R$  where  $OP$  is intersected by  $QV$  (9); so this point of intersection remains a fixed point during the whole of the motion. The quotient of the displacements of  $O$  and  $P$  is  $RO:RP$ , so  $RO:RP = a^2:b^2$ .

In order to find the nature of the rectified curve, making use of this fixed point  $R$ , we determine <sup>1)</sup> of  $PQ$ , considered as similar system, the points moving perpendicularly on their radius vector out of  $R$ ; these points  $T$  prove to be real for the ellipse and lie in such a way that  $\frac{PT}{TQ} = \pm \frac{b}{a}$ ; their distance to  $R$  remains constant during the whole of the motion; they describe a circle with centre  $R$ . If we produce  $RT$  till it intersects the  $x$ -axis in  $U$  and the  $y$ -axis in  $Y$ , then  $TU$  and  $UY$  also remain constant during the entire motion. From all this ensues that the rectified curve is an *epi- or hypocycloid* with  $R$  as centre;  $T$  describes the circle of the basis.

11. To find the length of the radii  $RT$  and  $\frac{1}{2} TU$  (fig. 7) expressed in the half axes  $a$  and  $b$  of the ellipse, we presuppose the figure in such a position where  $R$  has arrived in the production of the small axis; we make use here of the above given relations  $\frac{RP}{RO} = \frac{b^2}{a^2}$  and  $\frac{PT}{TQ} = \frac{b}{a}$ . Without any difficulty we find for the radius of the rolling circle

$$r = \frac{1}{2} TU = \frac{ab}{2(a+b)}$$

<sup>1)</sup> We give here for shortness'sake the results only.

and for the radius of the fixed one

$$R = RT = \frac{ab^2}{a^2 - b^2} = \frac{ab^2}{c^2}.$$

Moreover

$$\frac{R}{2r} = \frac{b}{a-b} \text{ en } \frac{R}{R+2r} = \frac{b}{a}.$$

For  $a = b$  (circle)  $R$  becomes equal to  $\infty$ , the rectified curve equal to a *cycloid*.

12. *Hyperbola on one of its axes as rectifying curve.* Let us first take the real axis as the axis of the arcs (fig. 8). As in 10 it is evident, that the point of intersection  $R$  of  $OP$  and  $QV$  is a fixed point during the whole of the motion, where  $\frac{RO}{RP} = -\frac{a^2}{b^2}$  ( $2a$  and  $2b$  real and imaginary axis of the hyperbola). The point  $T$  (10) is imaginary here; instead of this we consider the constant three-point logarithmic spiral whose rectifying curve  $WP$  is parallel to one of the asymptotes of the hyperbola.

Let us project both  $R$  and  $W$  (pole of the logarithmic spiral) on  $PQ$ , it then follows from the equation  $PR:RO = b^2:a^2$ , that the quotient of the projections of  $PR$  and  $RO$  is equal to  $\frac{b^2}{a^2}$ , and from the rectangular triangle  $PWQ$ , where  $PW:WQ = b:a$ , that the quotient of the projections of  $PW$  and  $WQ$  is likewise equal to  $b^2:a^2$ . So the projections of  $R$  and  $W$  coincide in  $L$ . So the tangent  $WQ$  of the trajectory ( $W$ ) (8) forms a constant angle  $W'WR = \angle WQO$  with the radius vector  $RW$ ; so the trajectory ( $W$ ) is a logarithmic spiral of the same shape as the constant describing logarithmic spiral ( $WP$ ), that is the curve ( $f$ ) is described by a constant logarithmic spiral which moves in threepoint contact with itself in such a way that its pole describes the same logarithmic spiral with opposite curvature.

Allowing for the modification of the figure we find that these considerations are literally the same for the hyperbola on the imaginary axis as the axis of the arcs. Of the additional geometric considerations to which the two kinds of spirals whose rectifying curves are hyperbolae give rise, we shall mention only that the two kinds of spirals are each other's evolutes and that both of them approach asymptotically logarithmic spirals of a definite position, with which they have a fourfold contact at infinity (the rectifying curves being the asymptotes of the hyperbola).

13. *Parabola on the axis as rectifying curve.* For the parabola (fig. 9) the centre  $O$  is at infinity; the considerations about the point  $R$  based on this centre do not hold good here. If we determine the radius of curvature of the evolute as a special case of a polar trajectory of a threepoint logarithmic spiral (8) by drawing  $QV \perp$  tangent  $PV$ , it is evident according to the properties of the parabola that this radius of curvature remains constant, equal to  $\mu$ , parameter of the parabola, because  $PI$  represents the length of the subnormal. So the evolute is a circle and the rectified curve ( $f$ ) an evolvent of the circle. Point  $R$  (point of contact of  $QV$ ) coincides here with  $I$ , because  $I$  is a fixed point of  $V$ . So it is situated here too on the right line ( $PI$ ) connecting  $I$  with the centre of the parabola.

14. *Tautochronism.* The condition that a motion along a given curve be tautochronous is: the tangential component of the force must be proportional to the length of the arc between the moving point to a point of the curve; in that case the motion takes place as a single oscillatory motion. For the curves whose rectifying curves are central conics (10, 12) where the force is supposed to act from the fixed point  $R$ ,  $RL$  (fig. 7, 8) is proportional to  $QO$  as  $b^2$  to  $c^2$  (10). In order that the motion along those curves be tautochronous with  $O$  as centre, the tangential component of the force must be proportional to  $RL$ , so the force itself (directed along  $RQ$ ) proportional to  $RQ$ , that is to the distance. So for a force acting from the centre  $R$  in proportion to the distance both curves are tautochronous. But the centre of tautochronism  $O$  is to be reached along the curve only in the cases of circle, ellipse or hyperbola ( $x$ -axis imaginary) as rectifying curves, so only cycloid, epi- and hypocycloid and the spiral of the second kind (rectifying curve a hyperbola on the imaginary axis) are in reality tautochrone; for the spiral of the first kind the centre of tautochronism does not lie on the curve, for the evolvent of the circle it lies at infinite distance. For the epicycloid the force must repel; for the hypocycloid and the spiral of the second kind it must attract.

For the cycloid point  $R$  lies at infinite distance; the force becomes constant and is directed according to the tangent in a cusp.

**Physiology.** — *“On the development of the myocard in Teleosts.”*

By Dr. J. BOEKE. (Communicated by Prof. T. PLACE.)

During the last few years much attention has been given to the structure of the heart muscle, and several investigators have stated the opinion, that the heart muscle of the vertebrate heart is not composed of definite cells, separated by clearly defined limits, but that the heart muscle forms a syncytium, in which no cell boundaries can be recognised. For the embryonic heart this is shown most completely by GODLEWSKI, independently from GODLEWSKI, but less fully by HOYER and HEIDENHAIN, confirmed and worked out by MARCEAU.

For the adult heart (homo, mammalia) it has been M. HEIDENHAIN<sup>1)</sup>, who has done most in this direction, and who has most strongly urged the conception of the heart muscle as a syncytium. According to him the septa, the “Treppen”, the delicate lines standing at right angles to the course of the myofibrillae, which are regarded by other investigators as cell-limits, have nothing to do with real intercellular structures (except perhaps from a phylogenetic point of view); they are “Schaltstücke”, portions of the musclefibre which remained as it were in an indifferent state, and play a part in the process of longitudinal growth of the fibres. For the still growing heart HEIDENHAIN draws the following conclusion: “dass die Schaltstücke ihrem ursprünglichen Verhalten nach wachsende Teile sind, Teile, welche das Längenwachstum besorgen und nach beiden Segmentenden hin das Material für die Angliederung neuer Muskelfächer liefern” (l. c. 1901 Pag. 69).

HOCHÉ<sup>2)</sup> on the other hand takes these “Schaltstücke”, for real cellular limits, though incomplete. He maintains that the Schaltstücke, the cement substance between the cells of the heart muscle, which according to EBERTH<sup>3)</sup> are homogeneous and after BROWICZ<sup>4)</sup> are in some cases homogeneous, in other cases composed of small rods arranged parallel to each other, separate the cells of the myocard, but only in the course of the myofibrillae. Between these “bâtonnets” “le sarcoplasme qui remplit les interstices des fibrilles se continue sans interruption apparente d’une cellule dans l’autre.” The small rods are lying just between the ends of the myofibrillae of the

1) Anat. Anzeiger Bd. XVI 1899. Anat. Anzeiger Bd. XX 1901.

2) Bibliogr. Anatomique 1897.

3) Arch. für path. Anat. und Physiologie, Bd. 37.

4) Virchow's Archiv. Bd. 139.

adjoining cells, which they bring in connection with each other. "Cette zone des bâtonnets constituerait donc . . . une réelle limite intercellulaire, mais une limite incomplète."

VON EBNER <sup>1)</sup> regards the cementlines, the "Schaltstücke", as broken-off perimysiummembranes, "abgerissene Perimysiumhäutchen".

SZYMONOWICZ reproduces in his textbook of histology, which appeared two years ago, a drawing of a section through the heart muscle of a hydropic cor, in which the myofibrillae of one cell are seen clearly to be in connection each with a fibrilla of the adjoining cell.

For the embryonic heart the disappearance of the cell boundaries has been described by several authors in different animals.

HEIDENHAIN <sup>2)</sup> reproduces a section through the heart of a duck embryo three days old, in which no traces of cellular limits are to be seen and the myofibrillae may be followed with great distinctness without interruption over a great area and the same fibrilla passing different nuclei.

According to HOYER <sup>3)</sup> in the cells of Purkinje the fibrillae (found only in the peripheral region of the cell body) may be followed without break through many cells. In young larvae of Triton HOYER found a complete absence of cell boundaries. According to this author the heart muscle is originally composed of isolated cells, but these cells fuse during the later stages of development, and the result is a syncytium.

That this is really the case is shown by GODLEWSKI. A preliminary communication <sup>4)</sup> appeared simultaneously with the paper by HOYER. In the elaborate study <sup>5)</sup> which appeared somewhat later, this process of fusion of the cells of the heart muscle in young rabbit and cavia embryos is described very fully. Here the cells of the myocard form at first a network composed of loosely arranged cells. By division and growth these cells get nearer to each other, and the intercellular protoplasmic bridges thicken, the intercellular spaces narrow; "dadurch verschmelzen die Zellen allmählig in eine einheitliche Masse, in welcher die Kerne zerstreut gelegen sind. . . Schliesslich stellt die Anlage des Herzmuskels eine *vollkommen einheitliche Protoplasmamasse* dar." In the protoplasm of this syncytium there appear small granules, staining deeply with iron-haematoxylin; during the next stages of development these granules arrange themselves in

<sup>1)</sup> Sitzungsber. Wiener Akademie. Math. naturw. Classe. Bd. 109 1900. Abth. III.

<sup>2)</sup> l. c. 1899 en 1901.

<sup>3)</sup> Bull. internat. de l'Acad. des Sciences de Cracovie 1899 Nov., 1901 Mars.

<sup>4)</sup> Bull. internat. de l'Ac. des Sc. de Cracovie Mars 1901.

<sup>5)</sup> Arch. f. mikrosk. Anat. Bd. 60, 1902.

rows (the same process was described by GODLEWSKI for the striped muscle fibres of the body muscles) and in this manner the delicate primitive histological myofibrillae are formed. In these originally homogeneous fibrillae during the course of development two elements appear, staining differently with iron-haematoxylin and eosin, the first sign of cross-striation, of the anisotropic and isotropic discs. The later stages of development and the appearance of the "Schaltstücke" were not studied by GODLEWSKI.

An essentially similar view has since been advocated by MARCEAU<sup>1)</sup> (1902). In a series of brief papers this author described the continuity of the heart muscle fibres in mammals, birds and lower vertebrates, and accepted in the main HEIDENHAIN's suggestion of the function of the "Schaltstücke" in the adult and the still growing heart.

In teleosts — I refer especially to the eggs of the Muraenoïdae, which provided me chiefly with the materials for the study of the processes I am about to describe here — the heart muscle cells are derived from the cells of the median portion of the walls of the pericardial cavity, which, as is the case in all anamnia, grow from either side underneath the entodermal tube and fuse with each other in the median line, so that a tube is formed between them, which opens at one end into the yolk-sac, at the other end into the arterial vessels, formed at the same time (ostium venosum and ostium arteriosum). Inside of this tube the endothelium of the heart is formed out of cells of the "masses intermédiaires" of the mesoderm of the head and partly out of cells which migrate from the region of the tail-knob towards the heart, and lay themselves against the myocard there where the heart tube opens into the yolk-sac.

In fig. 1 is reproduced a longitudinal section through the region of the heart of an embryo of *Muraena* N<sup>o</sup>. 1 with 38 pairs of muscle segments, which illustrates these features clearly. On the left side of the drawing the rostral end of the chorda is seen, and beneath the chorda the entoderm, which shows the widening of the oesophagus corresponding with the preopercular apertures, the primary gill-clefts. Between the entoderm and the periblast the heart is seen, and at the venous end of the heart tube lies a cluster of loose separate cells, which by their peculiar form and by the protoplasmic processes with which they (the greater part in the following sections), unite with the endothelium of the heart, appear as cells which aid to build up the endocard. The history of the genesis of the endocard however we will drop for the present, the repro-

<sup>1)</sup> C. R. de la Soc. de Biologie, T. 54, pag. 714—716, 981—984, 1485—1487; 1902.

duced drawing serving only to show the topographic relations. It is only the myocard that interests us here. The cells of those parts of the walls of the pericardial cavity that form the myocard, are distinctly separated at this stage of development, are of a cubical or cylindrical shape and very regular, as is shown in the figure. They possess a rather large round nucleus and have a granular looking protoplasm which shows no definite structure organisation. At both ends of the heart tube they gradually diminish in height until the flat shape of the cells of the other parts of the pericardial plates is reached.

The cell boundaries between the heart muscle cells are everywhere sharply defined; in preparations stained with iron-haematoxylin, at both sides of the heart tube (that turned towards the endocard and that turned towards the pericardial cavity) a delicate black line, following the cellular limits, is to be seen — the “Schlussleiste”.

The first signs of differentiation, which showed themselves in the heart muscle cells, tend already to give rise to a fibrillar structure. A granular stage, as described by GODLEWSKI, during which the protoplasm of the cells is full of deeply staining granules, which arrange themselves in rows and fuse to give rise to the myofibrillae, I have not been able to find. On the stage of the granular looking meshwork with small meshes, the usual appearance of protoplasm, there followed in my preparations immediately a stage, in which at the basal end of the cell (viz. that turned towards the endocard), extremely delicate fibrillae are to be made out, which in most cases run at right angles to the longitudinal axis of the heart tube.

These fibrillae, as far as could be made out, are homogeneous from the beginning, and do not give the impression of being composed of or derived from granules arranged in rows. However, this need not lead us to doubt the formation of the fibrillae in this way even here; the beautiful figures and clear descriptions of GODLEWSKI are too convincing on this point. Perhaps this stage lasts only a short time and is not represented in my preparations which are stained with iron-haematoxylin. Be this as it may, we only find the extremely delicate fibrillae<sup>1)</sup>, which thicken and become more distinct during the following stage. To this stage belong the sections drawn in fig. 2 and fig. 3 (longitudinal sections) and fig. 4 (cross section through the heart tube).

In order to understand these drawings rightly, the following may be of use. The heart is during this stage still lying as a straight

<sup>1)</sup> A regular network consisting of large protoplasmic discs as described by Mc CALLUM, I have never been able to find.

cylindrical tube in the direction of the embryonic axis, but always the heart tube deviates in its course somewhat to the right (or to the left). In longitudinal sections through the embryo the heart therefore is cut obliquely, and in the same section of  $4$  or  $5 \mu$  we are able to study the external half of the heart muscle cells (that is to say the side of the cells turned towards the pericardial cavity) at the venous end of the tube, the basal half of the adjoining cells, and then the endocardium and the median cross section of the heart muscle cells at both sides of the heart.

In fig. 3 are shown the two parts of the heart muscle cells as seen in one and the same section. The two parts of the figure are in the section continuous, but are lying in different optical planes. It was not possible however to reproduce the two parts in the same drawing, because in the section (thickness  $4 \mu$ ) different optical planes presented a different aspect of the same point. So I separated the two halves by a line, to indicate the point, where the drawing is made after a different optical section.

On the right side the cells of the myocard are seen from the side turned towards the pericardial cavity. They appear to be separated by distinct boundaries, are very regular, and show between the cells the black lines and meshes of the "Schlussleiste". On the left side of the figure the basal side of the heart muscle cells is to be seen. Because of the curved surface of the heart tube, at both sides the cells are seen in cross section, in the median part of the figure the basal part of the cells comes into view. In this part of the heart muscle cells the cell membranes have completely disappeared. There is only a mass of protoplasm to be seen, which has taken a faint stain with eosin; imbedded in it lie thin fibrillae stained black with iron-haematoxylin; these fibrillae run for the greater part at right angles to the heart axis round the heart-tube; some of them run more or less obliquely (fig. 3). The same fibrilla may be followed through more than one cell. At both sides the fibrillae curve round and run at right angles to the surface of the section. They present there a small point of a darker colour. The fibrillae are entirely homogeneous.

That these fibrillae are lying in reality only at the basal end of the cell is shown in fig. 2, in which a part of the myocardium is drawn as it appears in a median longitudinal section through the heart tube; as the fibrillae are running here at right angles to the optical plane, they appear as dots and where their course is more or less oblique, as short lines. In the corners of the cells we see (at the side of the cells turned towards the pericardial cavity) the black

dots of the "Schlussleisten". The cell boundaries cannot be followed now from one side of the wall to the other; at the basal side of the cells, there where the fibrillae are formed, the cell membranes have disappeared and the protoplasm of the cells is continuous. It seemed to me that the disappearance of the cell limits preceded the differentiation of the myofibrillae, on the other hand the question arises, whether the differentiation of the fibrillae does not give the impulse for the disappearance of the cell membranes. For in studying these cells closer, we sometimes find in cells, where only at the basal side of the cell the cellular membranes have disappeared, fibrillae lying there where the cells are still distinctly separated. These fibrillae do not pass from one cell to another, but end close to the cell-membrane with a small thickened point (fig. 3), and sometimes in two adjoining cells a pair of such fibrillae are seen just opposite to each other. In following stages of development in this part of the cells a greater number of fibrillae is to be found; these fibrillae then are seen to pass through different cells and the membranes of the cells have disappeared here too. These facts remind us of the appearance of the fibrillae on the boundaries of the myotomes (in longitudinal sections), and this being the beginning of the fusion of the fibrillae of the adjoining myotomes, the question arises, whether a similar process is going on in the heart muscle cells. Be this as it may, the fact remains, that only at that side of the cell in which the myofibrillae are formed, the membranes disappear and the protoplasma fuses.

We may call attention here to the fact, that the black meshes and lines of the "Schlussleiste" have disappeared at the basal side of the cells, there where the cell limits ceased to exist; at the other side of the cells, there where the cells are still sharply separated, they remain as clear and distinct as before.

In fig. 4 one half of a cross section through the heart tube is drawn, to demonstrate once more the course of the fibrillae and the structure of the myocard cells.

In the figure we see the endocardium (end.) composed of flattened cells, and around it the myocard <sup>1)</sup>. The fibrillae are here cut lengthwise, and may be followed without break through different cells. The cellular limits, seen in the outer half of the cell-body and absent in the inner half, we need not describe at length any more.

In preparations in which the centrosomes are stained in the other embryonic cells, in some cells of the myocard too they were visible

<sup>1)</sup> A pericardial membrane as a covering of the myocard, as it shows itself in salmon during the later stages of development, is not yet developed here. The heart lies entirely free inside the pericardial cavity.

as minute black granules (diplosomes) in the centre of an ovalshaped "heller Hof".

They were lying on the side of the nucleus in a rather indifferent position now on this side of the cell, than on that.

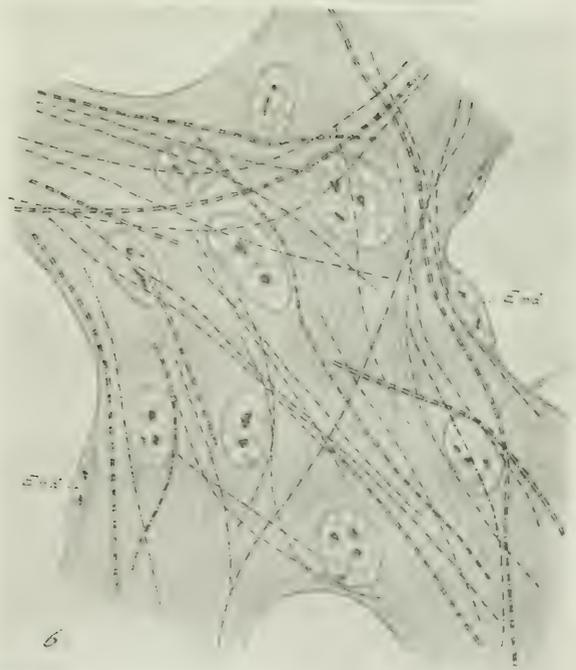
In the course of development the cells of the myocardium flatten more and more. The cell membranes disappear from between the cell bodies throughout the entire thickness of the myocard. In this stage the fibrillae are not so exclusively confined to the basal side of the cells, but are found more or less scattered throughout the cells. The greater part of the fibrillae, however, is still visible in the basal half of the heart muscle syncytium.

In fig. 5 a surface view (of the atrium) of such a myocard is drawn. Beneath the fibrillae we see three nuclei, no trace whatever of cell boundaries is visible. The course of the fibrillae is not so regular as it was before. They seem to be running now in different directions, although there is still one predominant course. This fact is due to the rate of growth of the heart tube being not the same in different directions. The heart has no more the shape of a simple cylindrical tube, but is differentiated already in sinus venosus, atrium and ventricle. With the growth of the different parts of the heart tube the displacing of the bundles of fibrillae goes hand in hand.

As shown in the figure, the myofibrillae of the heart now present a beautiful cross striation. But it must be noticed that the commencement of the functions of the heart muscle, of rhythmical peristaltic contractions coincides with the differentiation of the homogeneous fibrillae mentioned above. The differentiation of the fibrillae in isotropous and anisotropous discs takes place after the heart having contracted quite regularly for a long time already, and has nothing to do with the contractility of the fibrillae.

In this stage of development (the last stage which can be studied here, the muraenoid larvae invariably dying after having reached the critical period) the wall of the heart is still a simple membrane. The bundles of muscle fibres so characteristic for the adult vertebrate heart are not yet developed. For this reason I have reproduced in fig. 6 a part of a longitudinal section of the myocard of a larva of *Salmo fario* of 22 m.M., where the sponge-like structure of the myocard was established already. The myofibrillae, for the greater part arranged in bundles, may be followed over a great area past different nuclei of the myocard-syncytium. There is no trace of cellular limits, nor of "Schaltstücke" to be found.

So we must draw the conclusion, that in the case of teleosts too the myocard forms a syncytium, as maintained by GODLEWSKI,



*L. Baer del.*



HEIDENHAIN, HOYER and MARCEAU; that the myocard originally is formed of distinct cells, but that during the differentiation of the myofibrillae the cell limits of the myocard cells get lost, the cell bodies fuse and in this manner a syncytium is formed; that this disappearance of the cell membranes can be stated at first only there where the myofibrillae are formed, and that chronologically the formation of the fibrillae and the disappearance of the membranes coincide.

Where now the formation of this syncytium by a fusion of originally separated cells can be demonstrated in lower vertebrates and in the higher vertebrates, and the continuity of the fibrillae over a great area can be stated, there the hypothesis of HEIDENHAIN, that in the adult mammalian heart the "Schaltstücke" (cement lines) of the myocard which are not to be found in lower vertebrates and which appear in mammals in a relatively late stage of development, have nothing to do with cell limits, seems to have some truth in it. That this is of great importance for the physiology of the heart muscle, for the problem of the conduction of the impulse by the heart muscle fibres, I need only mention here.

As to the functions of the "Schaltstücke" we are, I think, still entirely in the dark, but for the hypothesis of HEIDENHAIN. This must be tested by further study. The study of the *later* stages of development of the mammalian heart with the use of the modern histological methods will throw more light upon this, as was pointed out already by GODLEWSKI. Perhaps the study of the structure of the muscular bridges, connecting the different parts of the mammalian myocard, too will throw some light upon this question.

#### DESCRIPTION OF THE FIGURES ON THE PLATE.

Fig. 1. Longitudinal section through the heart of an embryo of *Mur.* N<sup>o</sup>. 1 with 38 pairs of muscle segments. ph = pericardial cavity, m = myocard, e = endocard, per = periblast, ent = entoderm, ch = chorda, oes = oesophagus. Enl. = 240.

Fig. 2. Two cells of the myocard of an embryo of the same species of *Mur.* N<sup>o</sup>. 1 with 44 muscle segments. Longitudinal section, sublim.-formol, iron-haematoxylin and eosin. Enlarg. = 800.

Fig. 3. The same, cut tangentially. Enlarg = 800.

Fig. 4. Cross section through the heart of a slightly older embryo.

Fig. 5. Surface section of the wall of the atrium of a larva of *Mur.* N<sup>o</sup>. 1, five days old.

Fig. 6. Section through the wall of the ventricle of a larva of *salmo fario* of 22 mM. Enlarg. = 800.

**Mathematics.** Extract of a letter of Mr. V. WILLIOT, to the Academy.

In his splendid work entitled: "Théorie, propriétés, formules de transformation et méthodes d'évaluation des intégrales définies" Mr. BIJRENS DE HAAN takes as basis to determine the general formulae (143, 144, 145, 146) of page 134 a definite discontinuous integral the value of which has been established farther on in the work (Partie III, Méthode 9, N<sup>o</sup>. 16) at page 333 as

$$\int_0^{\infty} \sin(px) \cos(qx) \frac{dx}{x} = \begin{matrix} \frac{\pi}{2} \text{ for } p > q \\ \frac{\pi}{4} \text{ for } p = q \\ 0 \text{ for } p < q \end{matrix} \dots \dots \dots (1)$$

the value with respect to the discontinuity  $p = q$  being the mean of the extreme values.

But he gives this result on page 133 in the form:

$$\int_0^{\infty} \sin rx \cos qx \frac{dx}{x} = \begin{matrix} \frac{\pi}{2} \text{ for } q \leq r \\ 0 \text{ for } q > r \end{matrix}$$

so that in the continuation of his deduction we find that the term corresponding to  $q = r$  amounts to double the value of the real value and that the general formulae of page 134 are to be rectified in this way as well as the applications.

Particularly on page 639 formula 1900 we find

$$\int_0^{\infty} \frac{\sin x}{1 - 2p \cos x + p^2} \frac{\cos ax}{x} dx = \frac{\pi}{2p} \sum_a p^a = \frac{\pi}{2} \frac{p^{a-1}}{1-p},$$

whilst the exact value of this integral is

$$\frac{\pi}{2} \left[ \frac{p^{a-1}}{2} + p^a + p^{a+1} + p^{a+2} + \dots \right] = \frac{\pi}{4} p^{a-1} \frac{1+p}{1-p}.$$

And really writing after multiplication by  $p$ :

$$\int_0^{\infty} \frac{p \sin x}{1 - 2p \cos x + p^2} \frac{\cos ax}{x} dx = \frac{\pi}{4} p^a \frac{1+p}{1-p},$$

it is sufficient to develop the first factor of the function of which the integral is to be found

$$\frac{p \sin x}{1 - 2p \cos x + p^2} = \sum_{k=1}^{\infty} p^k \sin kx$$

to find by means of the integral (1) the development of the second term of the equation:

$$\frac{\pi}{4} p^a \frac{1+p}{1-p} = \frac{\pi}{2} \left[ \frac{p^a}{2} + p^{a+1} + p^{a+2} + \dots \right].$$

It was in looking for a way to place in a form of a definite integral the general term of the series of LAMBERT modified by CLAUSEN :

$$\frac{1+x^n}{1+x^{2n}} \cdot x^{a^2} = \frac{4}{\pi} \int_0^{\infty} \frac{\sin a \cos (n+1) a \, da}{1-2x^n \cos a + x^{2n} a}$$

that I found this error.

It is easily seen that the rectification has to be extended to the whole N°. 12 of the method 41 of which the above mentioned integral forms a part and to any other application of the general formulae of page 134.

This paper was given to Dr. J. C. KLUYVER, who made the following communication about it:

The remarks of Mr. WILLIOT are on the whole correct. In the "Exposé de la Théorie etc." of BIERENS DE HAAN we really find on page 639

$$\int_0^{\infty} \frac{\sin x}{1-2p \cos x + p^2} \cdot \frac{\cos ax}{x} dx = \frac{\pi}{2} \cdot \frac{p^{a-1}}{1-p}$$

and this is incorrect whether  $a$  is an entire number or not.

Mr. WILLIOT now gives as an answer

$$\frac{\pi}{4} p^{a-1} \frac{1+p}{1-p},$$

and that will do for  $a$  as an entire number.

In the meanwhile he might have observed that this result neither holds good for  $a$  (not an entire number) and that we find for any possible positive  $a$ :

$$p < 1: \quad \frac{\pi}{4} \cdot \frac{p^{[a-\delta]} + p^{[a+\delta]}}{1-p}$$

$$p > 1: \quad \frac{\pi}{4} \cdot \frac{p^{-[a-\delta]} + p^{-[a+\delta]}}{p(p-1)}$$

(Here  $[a]$  means the greatest entire number smaller than  $a$ ).



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday October 31, 1903.

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(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 31 October 1903, Dl. XII).

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C O N T E N T S.

J. D. VAN DER WAALS: "The equilibrium between a solid body and a fluid phase, especially in the neighbourhood of the critical state", p. 230.

J. J. VAN LAAR: "The possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances," (2nd Communication). (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM, p. 244. (With one plate).

H. W. BAKHUIS ROOZEBOOM: "The phenomena of solidification and transformation in the systems  $\text{NH}_4\text{NO}_3$ ,  $\text{AgNO}_3$  and  $\text{KNO}_3$ ,  $\text{AgNO}_3$ ", p. 259.

A. F. HOLLEMAN and J. POTTER VAN LOON: "The transformation of benzidine." p. 262.

H. RAKEN: "The transformation of diphenylnitrosamine into *p*-nitrosodiphenylamine and its velocity." (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 267.

W. H. JULIUS: "The periodicity of solar phenomena and the corresponding periodicity in the variations of meteorological and earthmagnetic elements, explained by the dispersion of light", p. 270.

HANS STRAHL: "The process of involution of the mucous membrane of the uterus of *Tarsius* spectrum after parturition." (Communicated by Prof. A. A. W. HUBRECHT), p. 302.

J. C. KLUYVER: "Series derived from the series  $\sum \frac{m(m)}{m}$ ", p. 305.

G. GRIJNS: "The Aescusform of *Aspergillus fumigatus* Fresenius." (Communicated by Prof. F. A. F. C. WENT), p. 312.

W. VAN BEMMELEN: "The daily field of magnetic disturbance." (Communicated by Dr. J. P. VAN DER STOK), p. 313.

J. H. BONNEMA: "A piece of Lime-stone of the Ceratopyge-zone from the Dutch Diluvium." (Communicated by Prof. K. MARTIN), p. 319.

S. HOOGWERFF and W. A. VAN DORP: "On the compounds of unsaturated ketones and acids", p. 325.

TH. H. BEHRENS: "The conduct of vegetal and animal fibers towards coal-tar-colours", p. 325.

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The following papers were read:

**Physics.** — *“The equilibrium between a solid body and a fluid phase, especially in the neighbourhood of the critical state.”*

By Prof. J. D. VAN DER WAALS.

After the publication of the experiments of Dr. A. SMITS in the proceedings of the September meeting, communicated by Prof. BAKHUIS ROOZEBOOM, I had a discussion with the latter chiefly on the question if and in what way the liquid equilibriums and the gas equilibriums which may exist by the side of a solid phase, must be thought to be connected by a theoretic curve at given temperature, in consequence of the continuity between liquid and gas. It is in agreement with the wish of Prof. BAKHUIS ROOZEBOOM, that I communicate the following observations.

Let us imagine the  $\psi$ -surface of a binary mixture, anthraquinone and ether, in which we will call ether the second substance, at a temperature slightly above  $T'_k$  for ether. Then there is a liquid-vapour plait, closed on the side for ether.

Let us add the  $\psi$ -curve or the  $\psi$ -surface for the solid state, the  $\psi$ -curve when the solid state has an invariable concentration. If only pure anthraquinone should be possible in the solid state, this  $\psi$ -curve would lie in the surface for which  $x=0$ . For the sake of perspicuity we shall start from this hypothesis in our first description. Then we find the phases which coexist with the solid anthraquinone, by rolling a plane over the  $\psi$ -surface and the conjugate  $\psi$ -curve.

On account of the slight compressibility of the solid body, we can describe a cone, unless the pressure be excessively high. This surface enables us to find the coexisting phases; its vertex lies viz. in the point  $x=0$ ,  $v=v_s$  and  $\psi=\psi_s$ , if  $v_s$  represents the molecular volume of the solid anthraquinone and  $\psi_s$  the value of the free energy, both at the temperature considered. The curve of contact of this cone and the  $\psi$ -surface represents then the coexisting phases. For shortness' sake we will use for it the name of contact-curve, though it is properly speaking also a connodal curve on the  $\psi$ -surface of the binary mixture having its second or conjugate branch on the  $\psi$ -surface of the solid state.

Now we can have three cases for the course of this contact-curve. 1<sup>st</sup>. It may remain wholly outside the liquid-vapour-plait, and will form then a perfectly continuous curve. 2<sup>nd</sup>. It may pass through that plait, in which case one part of this curve will represent gas phases and another liquid phases, which two parts will be connected by a third part lying between the two branches of the connodal

curve and representing metastable and unstable phases. 3<sup>rd</sup>. It may touch as intermediate case the connodal curve of the transverse plait in a point which will be the plaitpoint, as will appear presently.

As to the course of the liquid part of the contact-curve we may at once conclude, though this will be shown afterwards in a more striking way, that two cases may occur. From the point on the connodal curve where it enters the liquid part of the  $\psi$ -surface with increasing pressure, the curve will namely move more and more towards decreasing values of  $x$ , and finally terminate at  $x = 0$  or it can move towards increasing values of  $x$ .

If we trace the  $\psi$ -curve for  $x = 0$ , and add a portion of the

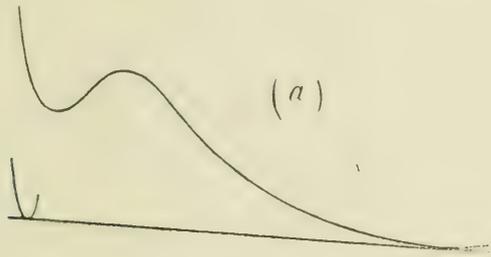


fig. 1 (a)

$\psi$ -curve for the solid body to the figure, then if this portion has position (a), so if the volume of the solid body is smaller than that of the liquid, only one bi-tangent can be drawn, and this will represent a coexisting gas phase. If on the other hand the added portion of the  $\psi$ -curve for the solid phase has position (b),

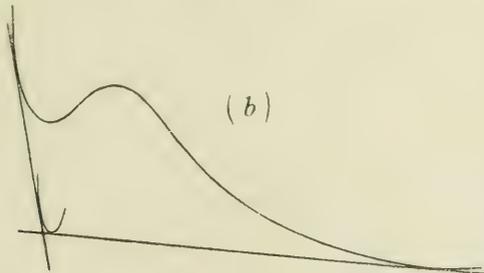


fig. 1 (b)

so if the volume of the solid phase is larger than that of the liquid, two bi-tangents may be drawn. At low pressure, a coexisting gas phase will exist, and at high pressure a coexisting liquid. In the latter case the liquid part of the contact-curve will move towards points for which  $x$  decreases when the pressure increases.

For a contact-curve which passes through the plait of the  $\psi$ -surface, the property holds of course good that the pressure is the same for the two points, in which it meets the connodal curve of the transverse plait. If namely a bi-tangent plane is made to roll simultaneously over the  $\psi$ -curve (or the  $\psi$ -surface) of the solid substance, and over the gas part of the  $\psi$ -surface of the binary mixture, then if this tangent plane meets a point of the binodal curve of the transverse plait, this tangent plane will also touch the  $\psi$ -surface in a point of the other branch of the binodal curve, and this point will represent a liquid phase. Three phases are then in equilibrium. The pressure that then prevails, is therefore the three-phase-pressure at given temperature. If the temperature should be such that the contact-curve no longer passes through the plait, then no three-phase pressure exists any longer for that value of  $T$ . For the intermediate case the solid body is in equilibrium with two phases, which have become equal and the two points of the connodal curve which the contact-curve has in common with it, have coincided in the plaitpoint.

Particulars as to the course of the contact curve are found from the differential equation of  $p$ , when  $x$  and  $T$  varies. If we represent the concentration and the molecular volume of the solid body by  $x_s$  and  $v_s$  and that of the coexisting phase, whether it be a gas phase or a liquid phase, by  $x_f$  and  $v_f$ , this equation may be brought under the following form, which is perfectly analogous to that which holds for the coexisting phases of a binary mixture :

$$v_{sf} dp = (v_s - v_f) \left( \frac{d^2 \xi}{dv_f^2} \right)_{p,T} dv_f + \frac{W_{sf}}{T} dT$$

For the signification of  $v_{sf}$  and  $W_{sf}$  I refer to Cont. II, p. 107 etc. If  $T$  is kept constant, we have for the course of  $p$  the differential equation :

$$v_{sf} \frac{dp}{dv_f} = (v_s - v_f) \left( \frac{d^2 \xi}{dv_f^2} \right)_{p,T}$$

As long as the contact-curve does not pass through the plait,  $\frac{d^2 \xi}{dv_f^2}$  is always positive.

If in the solid state only the pure first substance (in the case under consideration anthraquinone) should occur, then  $x_s = 0$ .

But the same differential equation holds also, if  $v_s$  should be variable. For the case of anthraquinone and ether the value of  $x$  in the gas phase is higher than that of the liquid phase for coexisting liquid and gas phases, or  $x_2 > x_1$ . It is therefore to be expected,

that the value of  $x_s$  in the solid state will a fortiori be smaller than that of the phase coexisting with it, whether the latter is a gas or a liquid phase. We do not wish to state positively that there are no exceptions to this rule. But for the case ether and anthraquinone we may safely assume that  $x_s - x_f$  is negative.

Now it remains only to know the sign of  $v_{sf}$ , to be able to derive the sign of  $\frac{dp}{dx_f}$ .

The expression  $v_{sf}$  stands in the place of  $(v_s - v_f) - (v_s - x_f) \left( \frac{dV_f}{dx_f} \right)_{p,T}$  and represents the decrease of volume per molecular quantity when an infinitely small quantity of the solid phase passes into the coexisting phase at constant pressure and constant temperature. If this coexisting phase should be a vapour phase, this decrease of volume is undoubtedly negative. But this quantity may also be positive, and if we make the series of pressures include all kinds of values, so if we make the pressure ascend from very low values up to very high ones, there is undoubtedly at least once reversal of sign, and for the case that the contact-curve under high pressure moves towards increasing values of  $x$  there is even twice reversal of sign.

To demonstrate this, we inquire first into the geometrical meaning of  $v_{sf}$ . Let the point  $P$  be the representation of the solid phase, with  $v_s$  and  $x_s$  as coordinates — and the point  $Q$  the representation of the coexisting fluid phase with  $v_f$  and  $x_f$  as coordinates. Let us draw through  $Q$  the isobar and let us determine the point  $P'$ , in which the tangent to this isobar of  $Q$  cuts the line which has been drawn through  $P$  parallel to the volume-axis, then  $-v_{sf} = PP'$ . If the point  $P'$  lies on the positive side of  $P$ , then  $v_{sf}$  is negative. For the special case that the tangent to the isobar of  $Q$  passes through  $P$ ,  $v_{sf} = 0$ . In the same way  $v_{sf}$  would be positive, if  $P'$  should lie on the negative side of  $P$ .

In order to know the sign of  $v_{sf}$ , the course of the curves of equal pressure must therefore be known. In my "Ternary systems" I (These proceedings Febr. 22<sup>nd</sup> 1902, p. 453) I have represented for the analogous case of a binary system, for which the second component has the lowest  $T_k$ , the course of the isobars by the line  $BEDD'E'B'$  in Fig. 2. I have added another isobar to the reproduction of this figure — and I have represented the solid phase by the point  $P_s$ . The added isobar passes through the plaitpoint. This isobar has an inflection point somewhat to the right of the plaitpoint. Each of these lines of equal pressure having an inflection point, there is a locus for these points, which I have left out in the



the other side of the isobars, it would no longer be possible to draw two tangents, and the locus for which, with regard to  $P_s$ , the value of  $v_{sf}$  is 0, would have but one branch.

Now, however, the point  $P_s$  is variable, first because the volume of the solid body depends on the pressure, and secondly when the concentration should change. This enhances of course the difficulty, if we wished to determine this locus. But this will not detract from the thesis that for the contact-curve, when it ascends from low pressure to high pressure, twice  $v_{sf}$  is 0, when the solid body has a smaller volume than it would have in fluid form at the same temperature and under the same pressure — and that only once  $v_{sf}$  is 0 in the opposite case. When  $P_s$  is variable, the locus for which  $v_{sf} = 0$ , is construed by drawing from every special position of  $P_s$  the tangents to the isobar of the pressure of  $P_s$ , and by joining the points of contact obtained in this way.

If the contact-curve does not pass through the plait, the value of  $v_{sf}$  is negative for the points outside the two branches of the locus  $v_{sf} = 0$ , and positive for the points inside.

If however the contact-curve passes through the plait, the value of  $v_{sf}$  is more complicated. In the figure the two tangents have been drawn to the isobar  $BEDD'E'B'$ ,  $P_s$  being supposed to be in the position that corresponds to the pressure of this line. In this case too the value of  $v_{sf}$  is negative for the points lying outside the two points of contact. For the points between the points of contact we cannot assume  $v_{sf}$  to be positive, however. This holds only till the points  $D$  and  $D'$  are reached. Between  $D$  and  $D'$ ,  $v_{sf}$  is again negative, and the transition from positive to negative takes place in the points  $D$  and  $D'$  through infinitely great.

In the same way the value of  $\left(\frac{d^2\xi}{dv_{sf}^2}\right)_{pT}$  is complicated for the points of a contact-curve, passing through the plait. I have stated this already in "Ternary systems" I, Proceedings February 22<sup>nd</sup> 1902 footnote p. 456. For the points between the connodal and the spinodal curve this quantity is still positive; for the points between the spinodal and the curve for which  $\frac{\partial^2\psi}{\partial v^2}$  is 0, it is negative; whereas for the points inside this last curve it is again positive. This last transition from negative to positive takes place through infinitely great.

Let us write the equation for the determination of  $\frac{dp}{dv_{sf}}$  in the following form:

$$\frac{\partial^2 \Psi}{\partial v_f^2} v_{sf} \frac{dp}{dx_f} = (x_s - x_f) \frac{\partial^2 \Psi}{\partial v_f^2} \frac{\partial^2 \xi}{\partial v_f^2}$$

or

$$\frac{\partial^2 \Psi}{\partial v_f^2} v_{sf} \frac{dp}{dx_f} = (x_s - x_f) \left\{ \frac{\partial^2 \Psi}{\partial x_f^2} \frac{\partial^2 \Psi}{\partial v_f^2} - \left( \frac{\partial^2 \Psi}{\partial x_f \partial v_f} \right)^2 \right\}.$$

In this way we simplify the discussion. The factor of  $x_s - x_f$  never becomes infinitely great in this case. This factor is then positive outside the spinodal curve and negative inside it. On the spinodal curve itself it is zero. As  $x_s - x_f$  is always negative in the case of anthraquinone and ether, the second member of the last equation is negative outside the spinodal curve and positive inside it. From this last equation follows: 1<sup>st</sup> that if we follow the contact-curve throughout its course, there exists a maximum and a minimum value for the pressure for the points lying inside the plait, that is when the spinodal curve is passed. 2<sup>nd</sup> that when  $v_{sf} = 0$ , the value of  $\frac{dp}{dx}$  is either twice or only once infinitely great. In the points where  $\frac{d^2 \Psi}{dv_f^2} = 0$ ,  $\frac{dp}{dx_f}$  has the value of  $\left( \frac{\partial p}{\partial x_f} \right)_c$ , as follows from the equation given if we put there  $\frac{\partial^2 \Psi}{\partial v_f^2} = 0$ , but which also follows directly from :

$$dp = \frac{\partial p}{\partial x_f} dx_f + \frac{\partial p}{\partial v_f} dv_f.$$

putting  $\frac{\partial p}{\partial v_f} = 0$ .

For contact-curves which pass through the plait not far from the plaitpoint, it appears clearly from the figure, that the points for which  $\frac{dp}{dx}$  is infinitely great, lie outside those for which  $\frac{d^2 \Psi}{dv_f^2} = 0$ . That is to say, that the locus for which  $v_{sf} = 0$ , lies outside the spinodal curve. In the neighbourhood of the top of the plait they lie even outside the connodal curve. Also for the isobar  $BEDD'E'B'$  I have drawn them in the figure given in such a way that the points of contact of tangents from  $P_s$  lie outside the spinodal curve. I have not yet been able to decide whether there are any exceptions. In the following figure (3) I have represented the relation between  $p$  and  $x_f$  for a contact-curve, assuming that the points of contact lie as I have drawn them in fig. 2, and as they are sure to lie, when we are in the neighbourhood of the plaitpoint. The gas phases which are in equilibrium with the solid body lie below  $B$ .

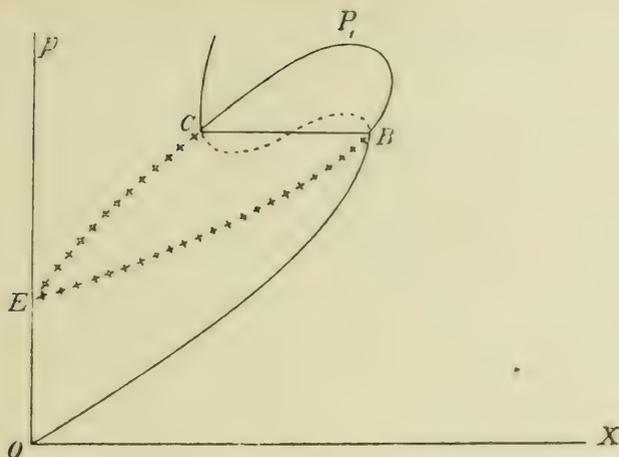


fig. 3

The liquid equilibria lie above  $C$ . The position of the line  $BC$  indicates the three-phase-pressure. The curve  $ECPBE$  denotes the liquid-vapour equilibria, of which the part lying below  $CB$  may only be realized by retardation of the appearance of the solid state.

Let us now examine what happens at higher temperature as well to the curve of the liquid-vapour equilibria as to that of the equilibria between the solid state and the fluid state. From the theory of the binary mixtures (Cont. II, p. 107 etc.) we know, that the first mentioned curve  $ECPBE$  contracts and moves upwards. If we assume  $dT$  to be infinitely small, all the points of this curve will be subjected to an infinitely small displacement, with the exception of one point, i. e. that for which  $W_{21} = 0$ . This point can lie on the right or on the left of the plaitpoint  $P$ , according as the plait-point curve descends or ascends. Also the curve of the solid and fluid equilibria is transformed and displaced. The modification which this curve undergoes with increase of temperature has been denoted by the dotted curve in fig. 4 and fig. 5. We shall presently explain this further. Now two cases may take place, which both occur for mixtures of anthraquinone and ether. Either the three-phase-pressure rises with  $T$ , or it falls. But in both cases such a temperature may occur that the straight line, which joins the two fluid phases coexisting with the solid body, has contracted to a point.

To the former of these two cases applies fig. 4. In this case the curve  $AB$  moves towards smaller values of  $x$  with increasing temperature. Not indefinitely, however. Near the highest value of  $T$ ,

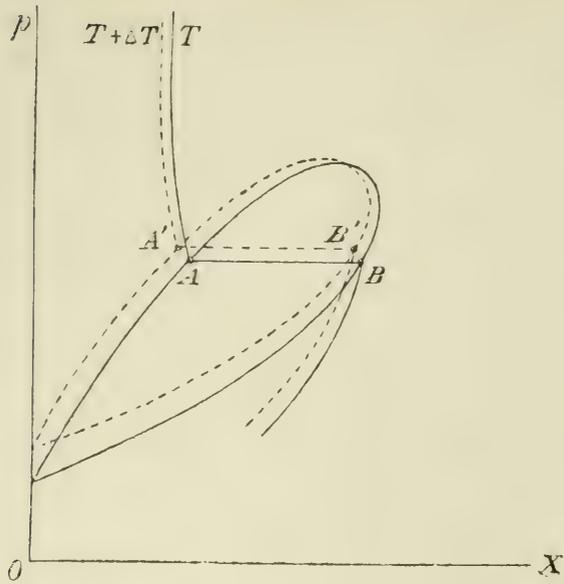


Fig. 4

the branches  $AA'$  and  $BB'$  have met, and so there is a minimum value for the value of  $x_A$ .

To the second case applies fig. 5. Then the curve  $AB$  will move to the right with decreasing temperature. With decreasing value of  $T$  the branches  $A'A$  and  $BB'$  will approach each other; and this

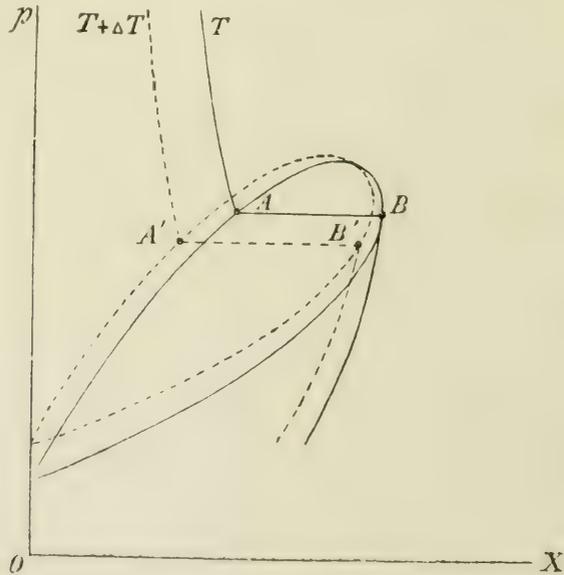


Fig. 5.

leads to the conclusion that there will be a maximum value of  $v_B$ . In fig. 6 the value of  $x$  for the two fluid phases of the three-phase-

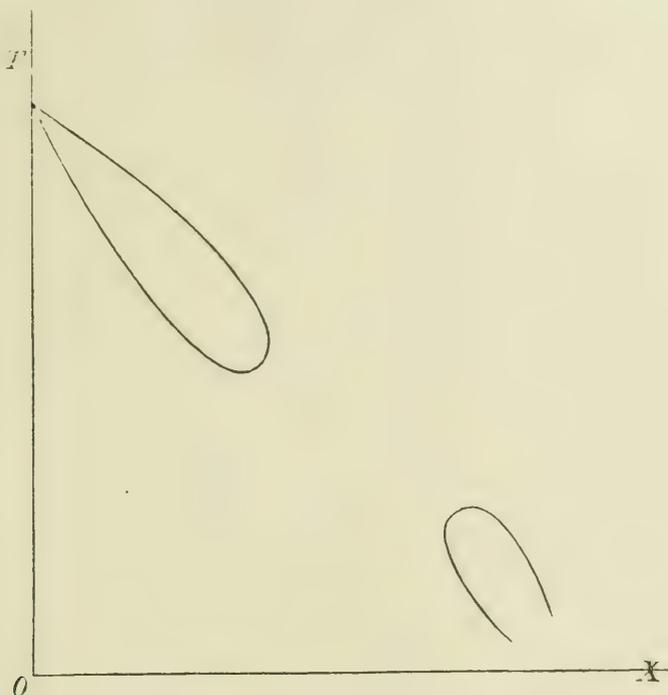


Fig. 6.

pressure as function of  $T$  is graphically represented. The highest temperature (the triple point of anthraquinone) applies to  $x = 0$ . The lowest point of the part of the  $x, T$  figure lying on the left is one plaitpoint and the highest point of the part of the  $x, T$  figure lying on the right is the second plaitpoint.

If we represented the relation between  $p$  and  $x$  for the fluid phases of the three-phase-equilibrium, we should also get two separate parts. It is easy to see that for smaller values of  $x$  an ascending closed branch is obtained, not unlike the closed  $p, x$  curve for a binary mixture at constant temperature — and that for higher values of  $x$ , a similar but descending curve is found.

The  $p, T$  projection for the three-phase-pressure, so of the curve according to which the two  $p, x, T$  surfaces intersect, consists of two separate curves, that for the higher temperatures being a descending curve, terminating in the  $p$  and  $T$  of the triple point of anthraquinone. The part for the lower temperatures is an ascending curve, beginning in the triple point of ether, if namely, we assume

perfect mixture also for the solid state. The two  $p, x, T$  surfaces meant in the preceding statement, are that for the coexistence of the two fluid phases with each other and that for the solid state and the fluid phases.

I shall proceed to give a few mathematical observations, which may serve to gain a better understanding of the whole phenomenon, and which are also required for the proof of some properties, which have been given above.

First the assumed deformation in the shape of the  $p, x$  curve (solid and fluid phase) for increase of temperature.

From the equation :

$$V_{sf} dp = (x_s - x_f) \left( \frac{\partial^2 \zeta}{\partial x_f^2} \right)_{p,T} dx_f + \frac{W_{sf}}{T} dT$$

follows that for constant  $x_f$  the equation holds :

$$T \left( \frac{dp}{dT} \right)_{x_f} = \frac{W_{sf}}{V_{sf}} = \frac{\frac{\partial^2 \psi}{\partial V_f^2} W_{sf}}{\frac{\partial^2 \psi}{\partial V_f^2} V_{sf}}$$

$W_{sf}$  being negative, the numerator of this expression is negative outside the curve for which  $\frac{\partial^2 \psi}{\partial v^2} = 0$ , and positive inside this curve.

The numerator is the same quantity as has been discussed before (p. 235). From this follows that for constant  $x_f$  the curve  $p, T$  has a tangent normal to the  $T$ -axis in two points, and between them two points, in which a maximum and a minimum value of  $p$  occurs — just as was the case with the  $p, x$  curve at constant temperature. One curve might be substituted for the other, but still, there is a difference. The  $p, x$  curve has its maximum and minimum coinciding in the plaitpoint. The  $p, T$  curve has it, when it runs through the point for which  $\frac{\partial^2 \psi}{\partial v^2}$  has two coinciding values equal to zero; so in the point which would be the critical point, when the binary mixture behaved as a simple substance.<sup>1)</sup> The consequence of this is, that if we trace the two  $p, T$  curves, (that for liquid and vapour and that for solid and fluid), these two curves intersect in the plaitpoint for the value of  $x$  of a plaitpoint, and that they do not touch as is the case with the  $p, x$  curves. Only for another value of  $x$  (the maximum

<sup>1)</sup> It has appeared to me that the course of the  $p, T$  curve requires further elucidation. I intend therefore to soon add some remarks on this subject to this communication.

and minimum discussed above) the two  $p, T$  curves touch. This point of contact yields of course an element for the three-phase-pressure.

The differential equation for the section of the two  $p, T, x$  surfaces, is found from the two relations which hold both at the same time :

$$v_{21} dp = (v_2 - v_1) \left( \frac{\partial^2 \xi}{\partial v_1^2} \right) dv_1 + \frac{w_{21}}{T} dT$$

and

$$v_{s1} dp = (v_s - v_1) \left( \frac{\partial^2 \xi}{\partial v_1^2} \right) dv_1 + \frac{w_{s1}}{T} dT.$$

We find then :

$$\frac{dp}{(v_s - v_1)v_{21} - (v_2 - v_1)v_{s1}} = \frac{\left( \frac{\partial^2 \xi}{\partial v_1^2} \right)_{pT} dv_1}{v_{s1}v_{21} - v_{21}v_{s1}} = \frac{dT}{T}$$

We shall shortly mention some obvious consequences. (1) If  $\left( \frac{\partial^2 \xi}{\partial v_1^2} \right)_{pT} = 0$ , the  $p, x$  and the  $T, x$  figure show a minimum or a maximum. So they exist for a plaitpoint. (2). For a maximum or minimum of  $x$ ,  $\frac{w_{21}}{v_{21}}$  must be  $\frac{w_{s1}}{v_{s1}}$ .

Now :

$$w_{21} = pv_{21} + \varepsilon_2 - \varepsilon_1 - (v_2 - v_1) \left( \frac{\partial \varepsilon_1}{\partial v_1} \right)_{pT}$$

and :

$$w_{s1} = pv_{s1} + \varepsilon_s - \varepsilon_1 - (v_s - v_1) \left( \frac{\partial \varepsilon_1}{\partial v_1} \right)$$

(See Cont. II p. 110). From this we derive :

$$\frac{\varepsilon_2 - \varepsilon_1}{v_2 - v_1} - \left( \frac{\partial \varepsilon_1}{\partial v_1} \right)_{pT} = \frac{\varepsilon_s - \varepsilon_1}{v_s - v_1} - \left( \frac{\partial \varepsilon_1}{\partial v_1} \right)_{pT} = \frac{\varepsilon_2 - \varepsilon_1}{v_2 - v_1} - \frac{\varepsilon_s - \varepsilon_1}{v_s - v_1}$$

$$\frac{v_2 - v_1}{v_2 - v_1} - \left( \frac{\partial v}{\partial v_1} \right)_{pT} = \frac{v_s - v_1}{v_s - v_1} - \left( \frac{\partial v}{\partial v_1} \right)_{pT} = \frac{v_2 - v_1}{v_2 - v_1} - \frac{v_s - v_1}{v_s - v_1}$$

This leads to  $\left( \frac{dp_{21}}{dT} \right)_x = \left( \frac{dp_{s1}}{dT} \right)_x = \frac{dp_{12s}}{dT}$  : or in words, the direc-

tion of the  $(p, T)_x$  curve for liquid and vapour, and that of the  $(p, T)_x$  curve for solid and fluid state are the same in the point of maximum and minimum value of  $x$  and the same as that of the  $p, T$  curve for the three-phase-pressure. The  $p, T$  curve of the three-phase-pressure descending with the temperature in the case of minimum  $x$  and vice versa, we conclude concerning the point of contact that in the first case it lies between critical point of contact and maximum pressure of the liquid vapour curve, in the second case on the vapour branch of the curve.

If we suppose that the two critical phases with which the solid body can coexist, and which differ considerably in concentration for anthraquinone and ether, approach each other, the two separate parts of the  $T, x$  figure and also that of the  $p, x$  figure and that of the  $p, T$  figure will approach each other. At the point of contact the two parts of the  $T, x$  figure, and that of the  $p, x$  figure will intersect at an acute angle. If we continue this modification further, the two upper branches of these figures have joined, forming one continuous curve; in the same way the two lower branches. Then the  $p, T$  curve shows a maximum. The existence of this maximum three-phase-pressure has already been demonstrated and discussed by me on the occasion of former investigations by prof. BAKHUIS ROOZEBOM<sup>1)</sup>. We find again the result obtained before, now under the following form:

$$\frac{p(v_2 - v_1) + \varepsilon_2 - \varepsilon_1}{v_2 - v_1} = \frac{p(v_s - v_1) - \varepsilon_s - \varepsilon_1}{v_s - v_1} = \frac{p(v_s - v_2) + \varepsilon_s - \varepsilon_2}{v_s - v_2};$$

which means, that if we write for that special point of the three-phase-pressure:

$$T \frac{dp}{dT} = \frac{\Delta w}{\Delta r},$$

the value of  $\Delta w$  would be 0.

If we now examine the course of the  $x, T$  curve for the three-phase-pressure more closely, making use of the formula on p. 241, or what comes to the same thing according to the formula of Verslag 1897, Deel 5, p. 491, it appears, that other complications may occur; and that it is not perfectly accurate to say that the  $p, T$  curve on the side of the anthraquinone is an ascending curve, till the triple point of this substance has been reached. Then we can also account for the asymmetric behaviour of the  $p, T$  curve. It ascends from the triple point of ether and descends on the other side.

In this consideration we shall denote by  $x_d, x_l$  and  $x_s$  the concentration of the vapour, of the liquid and of the solid body. In the same way we shall use  $\varepsilon_d, \varepsilon_l$  and  $\varepsilon_s$ ; then we get for a very small quantity of the admixture:

$$T \frac{dp}{dT} = \frac{\begin{array}{l} 1 \quad x_d \quad \varepsilon_d + pv_d \\ 1 \quad x_l \quad \varepsilon_l + pv_l \\ 1 \quad x_s \quad \varepsilon_s + pv_s \end{array}}{\begin{array}{l} 1 \quad x_d \quad v_d \\ 1 \quad x_l \quad v_l \\ 1 \quad x_s \quad v_s \end{array}} = \frac{\lambda(x_d - x_s) - (v_l - x_s)(r + \lambda)}{(x_d - x_s)(v_l - v_s) - (v_l - x_s)(v_d - v_s)} \quad ^2)$$

1) Verslag Kon. Akad. Amsterdam, 1885, 3e reeks, Deel 1, pag. 380.

2) The more accurate value of the numerator of the last fraction is:

$$(x_d - x_l) \{ \lambda_A (1 - x_s) + \lambda_B x_s \} - (v_l - x_s) \{ r_A (1 - x_d) + r_B x_d \}$$

In this we have, however, disregarded the heat of rarefaction,

We denote then the latent heat of liquefaction by  $\lambda$  and the heat of evaporation by  $v$ .

Let the principal component be anthraquinone at its triple point. If we add a very small quantity of ether,  $x_s$  and  $x_l$  and  $x_d$  will be small but  $x_d > x_l > x_s$ . We may even assume by approximation for this case, that no ether passes into the solid phase; hardly any will be found in the liquid, but most of it in the vapour. So  $x_s = 0$  and  $\frac{x_d}{x_l}$  is very great. For the limiting case which may be supposed, in which  $x_l$  would be zero, we have:

$$T \frac{dp}{dT} = \frac{\lambda}{v_l - v_s}$$

The initial direction of the  $\rho, T$  curve is that of the melting curve, and when  $v_l > v_s$ , this curve begins as an ascending curve with increasing temperature. But as soon as after further addition of ether the value of  $\frac{x_d - x_s}{x_d - x_s}$  has become equal to  $\frac{v_l - v_s}{v_d - v_s}$ , in which still a very small value of  $x_l$  is supposed, the numerator of the expression for  $T \frac{dp}{dT}$  is infinitely large and on further addition the sign of the numerator is reversed and the  $\rho, T$  curve is no longer ascending, but descending with increase of  $T$ .

Now let ether be the principal component. In this case we have to distinguish two different cases. 1<sup>st</sup>. Ether and anthraquinone are in solid state miscible in all proportions; then the solid substance which we must think present, is *solid ether* and we start from the triple point of ether. 2<sup>nd</sup>. For all equilibriums anthraquinone remains unmixed with ether. Then the temperature must be thought slightly above the triple point of ether.

In the first case, if at the triple point of ether a little of the so much less volatile substance, anthraquinone is added, it is to be expected neither in the vapour, nor in the solid body, but only in the liquid; then we find:

$$T \frac{dp}{dT} = \frac{r + \lambda}{v_d - v_s}$$

So an increase of  $\rho$  with  $T$ , as occurs in the case of equilibrium between vapour and solid, in concordance with the rule, that if two phases of a mixture in which more phases are present, are of the same concentration, the equilibrium conforms to these two phases.

In the second case, in which we think ether present in liquid and vapour state at slightly higher temperature than that of the

triple point, added anthraquinone in solid condition will not pass into the vapour state. Then  $x_s = 1$  and  $x_d = 0$ . We get:

$$T \frac{dp}{dT} = \frac{r - x_l(r + \lambda)}{v_l - v - x_l(v_d - v_s)}$$

The quantity  $\lambda$  is now the latent heat of liquefaction of anthraquinone.

For vanishing value of  $x_l$  we find increase of  $p$  with  $T$ , as is found in case of equilibrium between liquid and vapour. In neither of these cases the numerator can become equal to zero when a small quantity of the second substance is added to the principal substance.

But I shall not enter into more particulars, nor discuss the treatment of special circumstances. If they are brought to light by the experiment, they can necessarily be derived from the above formulae. Nor shall I discuss the  $v, x, T$  curves, which would lead to greater digressions. For this discussion we should have to make use of two equations, of which that for the coexistence of liquid and vapour occurs in Cont. II, p. 104. For the  $v, x$  projection of the three-phase-equilibrium we get for anthraquinone and ether two separate branches, lying outside the limits of the maximum and the minimum value of  $x$  mentioned above. When these two values of  $x$  coincide, these branches meet, intersecting at an acute angle; at further modification the two  $v, x$  curves, viz. those for liquid and vapour, will yield a highest and a lowest value for the volume; at any case the  $v, x$  curve for the vapour phase. As appeared in an oral communication, Dr. SMITS had already arrived at this result.

I shall conclude with pointing out, that cases of *retrograde solidification* must repeatedly occur, both when the temperature is kept constant with change of pressure and when the pressure is kept constant with change of temperature.

**Chemistry.** — “*The possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances.*” By J. J. VAN LAAR. (2<sup>nd</sup> communication). (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. My investigations concerning the possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances, communicated in the Proceedings of the meeting of the 27<sup>th</sup> of June 1903, have, apart from the different theoretical considerations, led to the following practical results.

a. When the latent heat of mixing in the *solid* phase  $\alpha' = q_1 \beta'$  is *great*, the *solid* phase contains but very little of the second component. The portion of the meltingpoint-curve which may be realized, has a course as in fig. 1 (see the plate). The curves  $T = f(x')$ , viz.  $Aa$  and  $Bb$  show *maxima* at  $m$  and  $n$ , which maxima descend gradually for smaller values of  $\beta'$  till they are below  $a$  and  $b$ , the maximum at  $n$  sooner than that at  $m$ . (fig. 2). [We leave for the moment out of consideration what happens below the horizontal line through the point  $C$ , the *eutectic* point: for this see my preceding communication].

b. For smaller values of  $\beta'$  we get the case of fig. 3, where the branch  $BC$  shows a *minimum*, no longer below the temperature of  $C$ , but exactly *at*  $C$ . Immediately after (i. e. when  $\beta'$  is still somewhat smaller), the meltingpoint-curve assumes a shape as in fig. 4.  $C$  remains the *eutectic* point, where the two branches of the meltingpoint-curve meet with a *break*. As appears from the figure, we have now got parts of the meltingpoint-curve, which may be *realized*, also *below* the point  $C$  (see also fig. 14 and 14a of the communication referred to).

It is however very well possible, that in the meantime the minimum at  $D$  has *already disappeared*, and then we get a course as is represented in fig. 5 (observed i. a. by HISSINK for mixtures of  $\text{AgNO}_3$  and  $\text{NaNO}_3$ , (see also fig. 14b l.c.).

c. For still smaller values of  $\beta'$  the curve  $T = f(x')$  becomes *continuously realizable*. The points  $b$  and  $a$  coincide in a point of inflection  $b, a$  with *horizontal* tangent (fig. 6), which point of inflection soon passes into one with an *oblique* tangent  $L$  (fig. 7), while in most cases it disappears afterwards altogether for still smaller values of  $\beta'$ . (fig. 8).

The break at  $C$  has disappeared in the case of fig. 6 and from this moment there is no longer question of a *eutectic* point, and the meltingpoint-curve assumes the perfectly continuous shape of fig. 7 and 8.

d. As has already been observed in  $b$ , also the minimum at  $D$  will sooner or later disappear. For very small values of  $\beta'$  we get then *always* a course as in fig. 9.

*Observation.* As has been elaborately demonstrated in the preceding paper, a maximum at  $A$  for *normal* components can *never* occur with *positive* values of the different absorbed latent heats of liquefaction and mixing (see p. 156 l.c.). When such a maximum is observed, as was done e. g. by F. M. JAEGER<sup>1)</sup> for two isomeric

<sup>1)</sup> Akademisch Proefschrift (1903), p. 173—174.

tribroomtoluols, this always points to difference in size of the molecules in the liquid and solid phase<sup>1)</sup>. In fact JAEGER, found that his isomers are very likely *bi-molecular* in the *solid* phase<sup>2)</sup>.

2. We may now put the question: When will the minimum at  $D$ , which will disappear in any case for values of  $\beta'$  smaller than those for which fig. 3 holds, disappear *before* the case of fig. 6, so that a course as in fig. 5 becomes possible; and when will it disappear *after* the case of fig. 6, as has been assumed in our figures 6 to 8.

To answer this question, we shall first state for what values of  $\beta'$  the case of fig. 6 occurs.

The point  $b, a$  lying then on the top of the curve  $\frac{\partial^2 \zeta'}{\partial x'^2} = 0$  at  $x' = 1/2$ <sup>3)</sup>, we have, besides the equations (2) for  $x' = 1/2$  (see p. 153 l. c.), also the relation  $\frac{\partial^2 \zeta'}{\partial x'^2} = 0$  or  $\frac{RT}{x'(1-x')} - 2\alpha' = 0$ , i. e. with  $R = 2$  the relation  $T = \alpha' x'(1-x')$ .

The condition sought is accordingly:

$$T = \frac{T_1 \left(1 - \frac{1}{4} \beta'\right)}{1 + \frac{RT_1}{q_1} \log \frac{0,5}{1-x}} = \frac{T_2 \left(1 - \frac{1}{4} \frac{q_1}{q_2} \beta'\right)}{1 + \frac{RT_2}{q_2} \log \frac{0,5}{x}} = \frac{1}{4} q_1 \beta'.$$

for which with regard to the fundamental equations, some simplifying hypotheses permissible for our purpose have been made, which may be found on page 152 of the paper mentioned.

Now we can solve ( $R = 2$ ):

$$\log \frac{0,5}{1-x} = \frac{2 \left(1 - \frac{1}{4} \beta' - \frac{1}{4} \frac{q_1}{T_1} \beta'\right)}{\beta'}; \quad \log \frac{0,5}{x} = \frac{2 \left(1 - \frac{1}{4} \frac{q_1}{q_2} \beta' - \frac{1}{4} \frac{q_2}{T_2} \frac{q_1}{q_2} \beta'\right)}{q_2 \beta'}$$

hence, as  $1-x + x = 1$ :

$$-2 \left[ \frac{1}{\beta'} - \frac{1}{4} \left(1 + \frac{q_1}{T_1} \beta'\right) \right] + \dots = -2 \left[ \frac{1}{q_1/q_2 \beta'} - \frac{1}{4} \left(1 + \frac{q_2}{T_2}\right) \right] = 2. \quad (1)$$

1) See p. 208 and 209 of the "Proefschrift", where JAEGER gives the proof of this thesis, which I had communicated to him in a letter.

2) See p. 208 and 194 of the "Proefschrift".

3) Only if we assume  $\alpha'_1 = \alpha'_2$  (so  $b_1 = b_2$ ), this parabolic curve will be *symmetric* and its top will be exactly at  $x' = 1/2$ .

and this is the equation, from which  $\beta'$  can be solved. Unfortunately however  $\beta'$  cannot be solved from this in an *explicit* form.

Now the minimum disappears, when (see p. 168, l. c.):

$$\beta' = \frac{T_2 - T_1}{T_1} \dots \dots \dots (2)$$

That this takes place exactly at the *same moment* as that at which the case of fig. 6 occurs, is expressed by the relation:

$$e^{-2 \left[ \frac{T_1}{T_1 - T_2} - \frac{1}{4} \left( 1 + \frac{q_1}{T_1} \right) \right]} + e^{-2 \left[ \frac{q_2 T_1}{q_1 T_1 - T_2} - \frac{1}{4} \left( 1 + \frac{q_2}{T_2} \right) \right]} = 2. (3)$$

If we write for shortness:

$$\frac{q_1}{T_1} = g_1 \quad ; \quad \frac{q_2}{T_2} = g_2 \quad ; \quad \frac{T_2}{T_1} = \lambda \left( \text{so } \frac{q_2}{q_1} = \frac{g_2}{g_1} \lambda \right),$$

the equation (3) becomes:

$$e^{-2 \left[ \frac{1}{1-\lambda} - \frac{1}{4} (1 + g_1) \right]} + e^{-2 \left[ \frac{g_2 \lambda}{g_1 (1-\lambda)} - \frac{1}{4} (1 + g_2) \right]} = 2. (3a)$$

where  $\lambda$  will always be  $< 1$  ( $T_2$  is assumed  $< T_1$ ).

It is now easy to see that there are always corresponding values of  $\lambda$ ,  $g_1$  and  $g_2$  to be found, which satisfy (3), so that the minimum may just as well disappear before as after the case of fig. 6. In order to define the limits of  $T_1$ ,  $T_2$ ,  $q_1$  and  $q_2$ , in which either the one or the other will occur, we shall express e. g.  $g_2$  in function of  $g_1$  and  $\lambda$ . We get then successively:

$$e^{\frac{1}{2} (1 + g_1) - \frac{2}{1-\lambda}} + e^{\frac{1}{2} (1 + g_2) - 2 \frac{g_2 \lambda}{g_1 (1-\lambda)}} = 2,$$

$$e^{\frac{1}{2} g_1 - \frac{2}{1-\lambda}} - e^{\frac{1}{2} g_2 - 2 \frac{g_2 \lambda}{g_1 (1-\lambda)}} = 2, \dots$$

$$\frac{1}{2} g_2 - 2 \frac{g_2 \lambda}{g_1 (1-\lambda)} = \log \left( 2 e^{-1/2} - e^{1/2} g_1 - \frac{2}{1-\lambda} \right).$$

so finally:

$$g_2 = \frac{\log \left( 2 e^{-1/2} - e^{1/2} g_1 - \frac{2}{1-\lambda} \right)}{\frac{1}{2} - \frac{2 \lambda}{g_1 (1-\lambda)}} \dots \dots \dots (4)$$

This will be equal to 0 (first limiting-value, as  $\frac{q_2}{T_2}$  cannot become  $< 0$ ), when

$$2e^{-1/2} - e^{1/2} \varphi_1 - \frac{2}{1-\lambda} = 1,$$

or

$$\frac{1}{2} \varphi_1 - \frac{2}{1-\lambda} = \log(2e^{-1/2} - 1) = -1,546,$$

so when

$$\varphi_1 = \frac{4}{1-\lambda} - 3,092$$

or

$$\varphi_1 = \frac{4\lambda}{1-\lambda} + 0,908 \quad (\varphi_2 = 0). \quad \dots \quad (5)$$

The quantity  $\varphi_2$  will be  $\infty$  (second limiting-value, as  $\frac{q_2}{T_2}$  may have all values up to  $\infty$ ), when

$$\frac{1}{2} - \frac{2}{\varphi_1} \frac{\lambda}{1-\lambda} = 0,$$

i. e. when

$$\varphi_1 = \frac{4\lambda}{1-\lambda} \quad (\varphi_2 = \infty). \quad \dots \quad (5a)$$

It is evident that the difference between the two limits of  $\varphi_1$  is exactly 0,91.

We have now the following survey for different values of  $\lambda$ .

	$\lambda = 0$	$\lambda = 1/4$	$\lambda = 1/2$	$\lambda = 3/4$	$\lambda = 1$
$\varphi_2 = 0$	$\varphi_1 = 0,91$	$\varphi_1 = 2,24$	$\varphi_1 = 4,91$	$\varphi_1 = 12,91$	$\varphi_1 = \infty$
$\varphi_2 = \infty$	$\varphi_1 = 0$	$\varphi_1 = 1,33$	$\varphi_1 = 4$	$\varphi_1 = 12$	$\varphi_1 = \infty$

From this we see, that  $\varphi_2 = \frac{q_2}{T_2}$  may have all values from 0 to  $\infty$ , but that the values of  $\varphi_1 = \frac{q_1}{T_1}$  are limited to an *interval*, which varies with the value of  $\lambda = \frac{T_2}{T_1}$ . The greater  $\lambda$  becomes, i. e. the more  $T_2$  approaches to  $T_1$ , the smaller this interval comparatively becomes; so the value of  $q_1$  required must then become larger and larger.

All this applies to the case that the minimum disappears at the same moment as in the case of fig. 6. It is easy to see that when the minimum disappears *before* the case of fig. 6 the value of  $\varphi_1$  will have to be *larger* than that which is determined by (4) for

given values of  $g_2$  and  $\lambda$ . The opposite case, i. e. that the minimum disappears *after* the case of fig. 6. will take place when  $g_1$  is *smaller* than that value.

For, when the minimum *has already disappeared*, the value of  $\beta'$  in fig. (6) will be *smaller* than  $\frac{T_1 - T_2}{T_1}$ . We must accordingly substitute a smaller value of  $\beta'$  in (1), or what comes to the same thing, give a higher value to  $T_2$ , i. e. increase the value of  $\lambda$ . But it is obvious from the above table that when  $\lambda$  increases, a *higher* value of  $g_1$  will correspond to the *same* value of  $g_2$ .

Let us take as first example  $T_1 = 1000$ ,  $T_2 = 500$ ,  $q_1 = 4500$  Gr. cal.,  $q_2 = 250$  Gr. cal.  $\lambda$  is therefore  $= \frac{1}{2}$ ,  $g_1 = 4,5$  and  $g_2 = 0,5$ . The value of  $g_1$  ranges therefore within the interval 4 to 4,91, which holds for  $\lambda = \frac{1}{2}$ , so that it is *possible*, that the minimum disappears *in the neighbourhood* of (or exactly in) the case of fig. 6. The condition for its disappearance *for* the value of  $\beta'$  corresponding to that case, would be that there corresponded to  $\lambda = \frac{1}{2}$ ,  $g_1 = 4,5$ , according to (4), a value of  $g_2$ , given by :

$$g_2 = \frac{\log(1,2131 - e^{-1,75})}{0,5 - \frac{1}{2}} = \frac{\log 1,0322}{\frac{1}{2}} = 0,571.$$

So to  $g_2 = 0,50$  corresponds a greater value of  $g_1$  than the one given, viz. 4,5. This value is therefore *too low*, and the minimum will disappear *after* the case of fig. 6.

Second example. Let  $T_1$  be again 1000,  $T_2$  be 500, but now  $q_1 = 3000$ ,  $q_2 = 1000$ .

We shall not have to execute any calculation now, as this value falls *beyond* the interval 4 to 4,91,  $g_1$  being 3 with  $\lambda = \frac{1}{2}$ ;  $g_1$  is *much too low* to be *able* to correspond with any value of  $g_2$  whatever, and again the minimum will have to disappear when the case of fig. 6 occurs.

If on the other hand  $T_1$  had been 1000,  $T_2 = 500$ ,  $q_1 = 5000$ ,  $q_2 = 2000$ , then it would be clear without any calculation, that now the minimum *has already disappeared* when the case of fig. 6 occurs,  $g_2 = 5$  now lying *beyond* the interval on the *high* side. A course as in fig. 5 therefore becomes now possible, when the value of  $\beta'$  lies between that of fig. 3 and fig. 6.

The case of fig. 5, observed among others by HISSINK in mixtures of  $\text{AgNO}_3$  and  $\text{NaNO}_3$ , belongs therefore to the *possibilities*, and can occur for given  $T_1$ ,  $T_2$  and  $q_2$ , as soon as  $q_1$  has a sufficiently *high* value, or what comes to the same thing, as soon as for given  $T_1$ ,  $T_2$  and  $q_1$  the quantity  $q_2$  has a sufficiently *low* value. The

value of  $\frac{q_2}{T_2}$  or  $\varphi_2$  must then be *smaller* than that calculated from (4). If we then find a negative value for  $\varphi_2$ , the case of fig. 5 is entirely excluded for the given values of  $T_1$ ,  $T_2$  and  $q_1$ . In the equation (4) we have therefore at any rate a *criterion* to determine whether or no the case of fig. 5 can occur, when the value of  $\beta'$  lies between those to which the figures 3 and 6 apply.

3. Another important question will be, when the point of inflection  $L$  with oblique tangent (fig. 7) will disappear, and whether it can still be present e. g. with  $\beta' = 0$ .

Let us for this purpose determine the values  $\frac{dT}{dx}$  and  $\frac{d^2T}{dx^2}$ .

We found before (i.e. p. 155):

$$\frac{dT}{dx} = -T \frac{(x-x') \frac{\partial^2 \zeta}{\partial x^2}}{(1-x')w_1 + x'w_2} ; \quad \frac{dT}{dx'} = -T \frac{(x-x') \frac{\partial^2 \zeta'}{\partial x'^2}}{(1-x)w_1 + xw_2},$$

where

$$\frac{\partial^2 \zeta}{\partial x^2} = \frac{RT}{x(1-x)} - 2a ; \quad \frac{\partial^2 \zeta'}{\partial x'^2} = \frac{RT}{x'(1-x')} - 2a',$$

$$w_1 = q_1 + ax^2 - a'x'^2 ; \quad w_2 = q_2 + a(1-x)^2 - a'(1-x')^2.$$

Hence we get:

$$\frac{dT}{dx} = -T \frac{(x-x') \left[ \frac{RT}{x(1-x)} - 2a \right]}{(1-x')w_1 + x'w_2} ; \quad \frac{dT}{dx'} = -T \frac{(x-x') \left[ \frac{RT}{x'(1-x')} - 2a' \right]}{(1-x)w_1 + xw_2}, \quad (6)$$

from which we see i. a., that when e.g.  $\frac{dT}{dx}$  has been calculated,  $\frac{dT}{dx'}$  can be found by substituting  $x'$  for  $x$ ,  $-T$  for  $T$ ,  $-a'$  for  $a'$  and  $-a$  for  $a$  and by then reversing the sign of the second member.

The same holds for  $\frac{d^2T}{dx^2}$ , when  $\frac{d^2T}{dx'^2}$  is determined. From (6) follows for the point  $A$ , where  $T = T_1$ ,  $x = x' = 0$ ,  $w_1 = q_1$ :

$$\left( \frac{dT}{dx} \right)_0 = -\frac{RT_1^2}{q_1} \left( 1 - \left( \frac{x'}{x} \right)_0 \right) ; \quad \left( \frac{dT}{dx'} \right)_0 = -\frac{RT_1^2}{q_1} \left( \left( \frac{x}{x'} \right)_0 - 1 \right). \quad (7)$$

The initial direction depends therefore on the limit of the value of  $\frac{x'}{x}$ . We found for this expression (i.e. p. 156):

$$\log \left( \frac{x'}{x} \right)_0 = \frac{1}{R} \left( \frac{q_2 + a - a'}{T_1} - \frac{q_2}{T_2} \right), \quad \dots \dots \dots (8)$$

from which appears, i. a. that for  $a' = \infty, \frac{w'}{v}$  approaches to  $e^{-\infty}$ , hence it approaches rapidly to 0.

Let us now differentiate the expression (6) for  $\frac{dT}{dx}$  with respect to  $x$ . We find then, logarithmically differentiated :

$$\frac{\frac{d^2 T}{dx^2}}{\frac{dT}{dx}} = \frac{\frac{dT}{dx}}{T} + \frac{x(1-x) \left(1 - \frac{dw'}{dx}\right) - (x-x')(1-2x) \frac{RT(x-x')}{x(1-x)} \frac{dT}{dx} - 2a \left(1 - \frac{dw'}{dx}\right)}{(x-x') \left(\frac{RT}{x(1-x)} - 2a\right)} - \frac{(w_2 - w_1) \frac{dw'}{dx} + (1-x') \frac{dw_1}{dx} + x' \frac{dw_2}{dx}}{(1-x') w_1 + x' w_2}$$

We find therefore for  $T = T_1, x = x' = 0$ , where therefore  $\frac{RT}{x(1-x)} - 2a$  may be replaced by  $\frac{RT}{x(1-x)}$ , and where  $\frac{dw_1}{dx}$  is evidently 0 :

$$\left(\frac{d^2 T}{dx^2}\right)_0 = \left(\frac{dT}{dx}\right)_0 \left[ \frac{1}{T_1} \left(\frac{dT}{dx}\right)_0 + \frac{x(1-x) \left(1 - \frac{dw'}{dx}\right) - (x-x')(1-2x)}{x(x-x')} + \frac{1}{T_1} \left(\frac{dT}{dx}\right)_0 - \frac{2ax \left(1 - \frac{dw'}{dx}\right)}{(x-x') RT_1} - \frac{(w_2 - w_1) \frac{dw'}{dx}}{w_1} \right]$$

Now we must calculate the value of  $\left(\frac{dw'}{dx}\right)_0$ .

From (6) follows immediately :

$$\frac{dw'}{dx} = \frac{\frac{RT}{x(1-x)} - 2a}{\frac{RT}{x'(1-x')} - 2a'} \cdot \frac{w_1 + x(w_2 - w_1)}{w_1 + x'(w_2 - w_1)} \dots \dots \dots (a)$$

or

$$\frac{dw'}{dx} = \frac{x'(1-x')}{x(1-x)} \frac{1 - \frac{2ax(1-x)}{RT}}{1 - \frac{2a'x'(1-x')}{RT}} \cdot \frac{1 + x \frac{w_2 - w_1}{w_1}}{1 + x' \frac{w_2 - w_1}{w_1}}$$

hence for  $T = T_1$ :

$$\left(\frac{dw'}{dx}\right)_0 = \frac{x'}{x} \left(1 + \frac{(x-x')}{RT_1}\right) \left(1 + \frac{2a'x' - 2ax}{RT_1}\right) \left(1 + (x-x') \frac{w_2 - w_1}{w_1}\right)$$

or ( $R = 2$ ):

$$\left(\frac{dx'}{dx}\right)_0 = \frac{x'}{x} \left[ 1 + \frac{\alpha'x' - \alpha x}{T_1} + (x-x') \frac{w_2}{w_1} \right].$$

So this approaches to  $\frac{x'}{x}$ , but as will appear presently, for the determination of the term

$$x(1-x) \left( 1 - \frac{dx'}{dx} \right) - (x-x')(1-2x)$$

we must also retain the terms of lower order, as those of higher order disappear. We have further :

$$\begin{aligned} x \left( 1 - \frac{dx'}{dx} \right) &= (x-x') - x' \left[ \frac{\alpha'x' - \alpha x}{T_1} + (x-x') \frac{w_2}{w_1} \right] = \\ &= (x-x') \left[ 1 - x' \left\{ \frac{\alpha'x' - \alpha x}{(x-x')T_1} + \frac{w_2}{w_1} \right\} \right] = (x-x')(1-\Delta). \end{aligned}$$

The term mentioned becomes therefore :

$$(x-x') \left( (1-x)(1-\Delta) - (1-2x) \right) = (x-x')(x-\Delta).$$

Hence we get :

$$\left(\frac{d^2T}{dx^2}\right)_0 = \left(\frac{dT}{dx}\right)_0 \left[ \frac{2}{T_1} \left(\frac{dT}{dx}\right)_0 + \frac{x-\Delta}{x} - \frac{\alpha x \left( 1 - \frac{x'}{x} \right)}{(x-x')T_1} - \frac{x'w_2 - w_1}{xw_1} \right].$$

or introducing the value of  $\Delta$ , and of  $\left(\frac{dT}{dx}\right)_0 = -\frac{2T_1^2}{q_1} \left( 1 - \frac{x'}{x} \right)$  :

$$\begin{aligned} \left(\frac{d^2T}{dx^2}\right)_0 &= \left(\frac{dT}{dx}\right)_0 \left[ -\frac{4T_1}{q_1} \left( 1 - \frac{x'}{x} \right) + 1 - \frac{x'}{x} \left[ \frac{\alpha'x' - \alpha x}{(x-x')T_1} + \frac{w_2}{w_1} \right] - \frac{\alpha}{T_1} - \frac{x'w_2 - w_1}{xw_1} \right] = \\ &= \left(\frac{dT}{dx}\right)_0 \left[ -\frac{4T_1}{q_1} \left( 1 - \frac{x'}{x} \right) - 2 \frac{x'w_2}{xw_1} + \frac{x'}{x} - \frac{x'}{x} \frac{\alpha'x' - \alpha x}{(x-x')T_1} + 1 - \frac{\alpha}{T_1} \right] = \\ &= \left(\frac{dT}{dx}\right)_0 \left[ \left( 1 - \frac{\alpha}{T_1} - \frac{4T_1}{q_1} \right) + \frac{x'}{x} \left\{ 1 + \frac{4T_1}{q_1} - 2 \frac{w_2}{w_1} - \frac{\alpha'x' - \alpha x}{(x-x')T_1} \right\} \right]. \end{aligned}$$

Now  $(w_2)_0 = q_2 + \alpha - \alpha'$ ,  $(w_1)_0 = q_1$ , so that we finally get :

$$\begin{aligned} \left(\frac{d^2T}{dx^2}\right)_0 &= \frac{1}{q_1} \left(\frac{dT}{dx}\right)_0 \left[ q_1 \left( 1 - \frac{\alpha}{T_1} \right) - 4T_1 + \left(\frac{x'}{x}\right)_0 \left\{ q_1 + 4T_1 - 2(q_2 + \alpha - \alpha') - \right. \right. \\ &\quad \left. \left. - \frac{\alpha'}{T_1} \left(\frac{x'}{x}\right)_0 - \alpha \right\} \right] \dots \dots \dots (9) \\ &\quad \left. 1 - \left(\frac{x'}{x}\right)_0 \right] \end{aligned}$$

where  $\left(\frac{x'}{x}\right)_0$  has the value given in (8).

This expression for  $\left(\frac{d^2T}{dx^2}\right)_0$  is still very complicated, even after the great simplifications, which attend the introduction of  $x = x' = 0$ .

Besides by a direct calculation, the corresponding value for  $\left(\frac{d^2T'}{dx'^2}\right)_0$  may also be found by changing letters and signs as mentioned above, and the latter method is even the easier. Then we get:

$$\left(\frac{d^2T'}{dx'^2}\right)_0 = \frac{1}{q_1} \left(\frac{dT'}{dx'}\right)_0 \left[ q_1 \left(1 - \frac{\alpha'}{T_1}\right) - 4T_1 + \left(\frac{x}{x'}\right)_0 \left\{ q - 4T_1 - 2q_1 + \alpha - \alpha' \right\} - \frac{q_1}{T_1} \frac{\alpha' - \alpha \left(\frac{x'}{x'}\right)_0}{\left(\frac{x}{x'}\right)_0 - 1} \right] \dots \dots \dots (9a)$$

In the discussion of the two quantities  $\left(\frac{d^2T}{dx^2}\right)_0$  and  $\left(\frac{d^2T'}{dx'^2}\right)_0$ , two limiting cases are chiefly worthy of consideration, viz.  $\alpha' = \infty$  and  $\alpha' = 0$ . Let us further always put  $\alpha$  (latent heat required for the mixing of the liquid phase) = 0.

a. For  $\underline{\alpha' = \infty}$   $\frac{x'}{x}$  becomes exponentially = 0, hence

Lim.  $\left(\alpha' \frac{x'}{x}\right)_0$  will be 0. The two expressions are then transformed into:

$$\left(\frac{d^2T}{dx^2}\right)_0 = \frac{1}{q_1} \left(\frac{dT}{dx}\right)_0 \left[ q_1 - 4T_1 + \left(\frac{x'}{x}\right)_0 \alpha' \left\{ 2 - \frac{q_1}{T_1} \left(\frac{x'}{x}\right)_0 \right\} \right]$$

$$\left(\frac{d^2T'}{dx'^2}\right)_0 = \frac{1}{q_1} \left(\frac{dT'}{dx'}\right)_0 \left[ -\frac{q_1}{T_1} \alpha' + \left(\frac{x}{x'}\right)_0 \alpha' \left\{ 2 - \frac{q_1}{T_1} \left(\frac{x'}{x}\right)_0 \right\} \right]$$

i. e. into:

$$\left(\frac{d^2T}{dx^2}\right)_0 = \frac{1}{q_1} \left(\frac{dT}{dx}\right)_0 (q_1 - 4T_1)$$

$$\left(\frac{d^2T'}{dx'^2}\right)_0 = \frac{1}{q_1} \left(\frac{dT'}{dx'}\right)_0 \times 2\alpha' \left(\frac{x}{x'}\right)_0 = -\infty$$

These expressions teach us, that in case the solid phase contains very little or nothing of the second component,  $\left(\frac{d^2T}{dx^2}\right)_0$  becomes 0, when  $q_1 = 4T_1$ . In this case therefore the point of inflection appears in the curve  $T_2 f'(x)$  exactly at  $x = 0$ .

$\left(\frac{dT}{dx}\right)_0$  being negative,  $\left(\frac{d^2T}{dx^2}\right)_0$  will also be *negative* if  $q_1 > 4T$ .

The meltingpoint curve will then turn its *concave* side to the  $x$ -axis at  $A$ , and *no* point of inflection will occur. This is in perfect agreement with what we found in our former paper.<sup>1)</sup>

As to  $\left(\frac{d^2T}{dx'^2}\right)_0$ , we see that this expression, just as  $\left(\frac{dT}{dx'}\right)_0$  will always be *negatively large*. For great  $a'$  the concave side of the curve  $T = f(x')$ , running almost vertically downward, is turned towards the  $x$ -axis, but the curve  $T = f(x')$  finally touching the ordinate  $x = 0$  asymptotically at  $T = 0$ , a point of inflection must at any rate be present *beyond* the maximum of the curve  $T = f(x')$  (see fig. 1; at  $L$ ).

This point of inflection  $L$  will occur immediately after the maximum at  $m$  for large values of  $a'$ , and these two points gradually approach the point  $A$ , where  $T = T_1, x' = 0$ .

As to the maximum  $m$ , this is of course represented by

$(1-x)w_1 + xw_2 = 0$  (see (6)) or  $x = \frac{w_1}{w_1 - w_2}$ . Now  $w_1 = q_1 - a'x^2 = q_1$ , and  $w_2 = q_2 - a'(1-x)^2 = -a'$ , when  $a'$  is large and  $x'$  very small; hence the maximum occurs at

$$x'_m = \frac{q_1}{q_1 + a'} = \frac{q_1}{a'} = \frac{1}{\beta'} \dots \dots \dots (11)$$

If therefore  $\beta'$  approaches to  $\infty$ , then  $x'_m$  (so also  $x'_m$ ) approaches to 0.

As to the point of inflection at  $L$ , the following remarks hold good for it.

From the expression for  $\frac{dx'}{dx}$  (see (a)) follows, when  $a = 0$  and  $a'$  is large :

$$\frac{dT}{dx'} = \frac{dT}{dx} \frac{x(1-x)}{x'(1-x')} \frac{w_1}{w_1 + x(w_2 - w_1)} = \frac{dT}{dx} \frac{x(1-x)}{x'} \frac{q_1}{q_1 - ax'} = \frac{dT}{dx} \frac{x(1-x)}{x'} \frac{1}{1 - \beta'x} \dots (b)$$

At small  $x'$  we get :

$$T = \frac{T_1}{1 - \frac{RT_1}{q_1} \log(1-x)}$$

hence :

$$\frac{dT}{dx} = - \frac{T_1 RT_1}{N^2 q_1} \frac{1}{1-x} = - \frac{RT_1^2}{q_1} \frac{1}{(1-x)(1 + 2\theta x)}$$

as  $N^2 = (1 - \theta \log(1-x))^2 = (1 + \theta x + \dots)^2 = (1 + 2\theta x)$ .

<sup>1)</sup> These proceedings, Febr. 25th 1902, p. 427; June 24th 1903, p. 29-30.

We have therefore :

$$\frac{dT}{dx'} = - \frac{RT_1^2 \cdot x}{q_1 \cdot x' (1 + 2\theta \cdot x)(1 - \beta'x)} = - \frac{RT_1^2 \cdot x}{q_1 \cdot x' (1 - \beta'x)}$$

when  $\beta'$  is great with respect to  $\theta$ , and hence :

$$\frac{d^2T}{dx'^2} = - \frac{RT_1^2 \cdot x' (1 - \beta'x) \frac{dx}{dx'} - x \left( 1 - \beta'x - \beta'x' \frac{dx}{dx'} \right)}{q_1 \cdot x'^2 (1 - \beta'x)^2}$$

Consequently this is 0, when

$$x' (1 - \beta'x) \frac{dx}{dx'} = x \left( 1 - \beta'x - \beta'x' \frac{dx}{dx'} \right)$$

Now we may write for  $\frac{dx}{dx'}$  (see (b)) :

$$\frac{dx}{dx'} = \frac{x(1-x)}{x' (1 - \beta'x)}$$

so that  $\frac{d^2T}{dx'^2} = 0$ , when

$$x(1-x) = x \left( 1 - \beta'x - \frac{\beta'x(1-x)}{1 - \beta'x} \right)$$

or

$$1-x = 1 - \beta'x \left( 1 + \frac{1-x}{1 - \beta'x} \right)$$

or

$$1 = \beta' \left( 1 + \frac{1-x}{1 - \beta'x} \right) = \beta' \left( 1 + \frac{1}{1 - \beta'x} \right)$$

From this we find :

$$1 - \beta'x = \frac{\beta'}{1 - \beta'} = -1,$$

so finally :

$$x_L = \frac{2}{\beta'}, \dots \dots \dots (12)$$

being the value of  $x$ , at which for large values of  $\beta'$  the point of inflection will be situated after the maximum at  $x = \frac{1}{\beta'}$  (see (11)).

So this value of  $x$  too approaches to 0, when  $\beta'$  approaches to  $\infty$ .

It is now evident that according to (10) for large values of  $\beta'$  the quantity  $\left( \frac{d^2T}{dx'^2} \right)_0$  approaches to  $-\infty$ . For already in the *immediate* neighbourhood of A the direction of the curve  $T = f(x')$ , which was initially *almost* vertical, changes into a *perfectly* vertical direction at the maximum.

b) The other limiting case is  $\underline{a' = 0}$ . The expressions (9) and (9a) take then the form

$$\left(\frac{d^2T}{dx^2}\right)_0 = \frac{1}{q_1} \left(\frac{dT}{dx}\right)_0 \left[ q_2 - 4T_1 + \left(\frac{x'}{x}\right)_0 \left\{ q_1 + 4T_1 - 2q_2 \right\} \right]$$

$$\left(\frac{d^2T}{dx'^2}\right)_0 = \frac{1}{q_2} \left(\frac{dT}{dx'}\right)_0 \left[ q_1 + 4T_1 + \left(\frac{x'}{x}\right)_0 \left\{ q_2 - 4T_1 - 2q_2 \right\} \right]$$

or

$$\left(\frac{d^2T}{dx^2}\right)_0 = \frac{1}{q_1} \left(\frac{dT}{dx}\right)_0 \left[ (q_2 - 4T_1) - \left(\frac{x'}{x}\right)_0 (q_2 - 4T_1) - 2(q_1 - q_2) \right] \quad (a'=0), (13)$$

$$\left(\frac{d^2T}{dx'^2}\right)_0 = \frac{1}{q_2} \left(\frac{dT}{dx'}\right)_0 \left[ (q_1 + 4T_1) - \left(\frac{x'}{x}\right)_0 (q_1 + 4T_1) - 2(q_1 - q_2) \right]$$

where according to (8) the limit of the proportion  $\left(\frac{x'}{x}\right)_0$  is represented by

$$\left(\frac{x'}{x}\right)_0 = e^{-\frac{q_2}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)} \dots \dots \dots (14)$$

We see from these expressions, that even with  $\beta' = 0$  a *point of inflection at  $x = 0$*  (and so also *before it*) is possible for the *two* curves  $T = f(x)$  and  $T = f(x')$ . For this it is required for the curve  $T = f(x)$ , that

$$\left(\frac{x'}{x}\right)_0 = \frac{q_1 - 4T_1}{(q_1 - 4T_1) - 2(q_1 - q_2)} = \frac{1}{1 - 2 \frac{q_1 - q_2}{q_1 - 4T_1}}$$

or

$$\frac{q_2}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \log \left( 1 - 2 \frac{q_1 - q_2}{q_1 - 4T_1} \right).$$

If  $2 \frac{q_1 - q_2}{q_1 - 4T_1}$  is not large, we may write for it by approximation :

$$2 \frac{q_2}{T_1 T_2} (T_1 - T_2) = 2 \frac{q_1 - q_2}{4T_1 - q_1}$$

We see that in any case  $\frac{q_1 - q_2}{4T_1 - q_1}$  must be *positive*.

The condition may now be written as follows :

$$\frac{q_1 - q_2}{q_2} = \frac{(4T_1 - q_1) (T_1 - T_2)}{4T_1 T_2} = \left( 1 - \frac{q_1}{4T_1} \right) \left( \frac{T_1}{T_2} - 1 \right),$$

or

$$\frac{q_2}{q_1} = \frac{T_2}{T_1} - \frac{q_1}{4T_1} \left( \frac{T_2}{T_1} - 1 \right).$$

hence

$$\frac{q_1}{4T_1} = \frac{\frac{T_1 - q_1}{T_2 - q_2} \dots \dots \dots (15)}{T_2 - 1}$$

If e.g.  $T_1 = 1100$ ,  $T_2 = 900$ ,  $q_1 = 2200$ ,  $q_2 = 1980$ , the first member is  $1/2$ , the second member  $\frac{11/3 - 10/3}{11/3 - 1}$ , so also  $1/2$ . [The term  $2 \frac{q_1 - q_2}{q_1 + 4T_1}$  under the *log*-sign is here  $\frac{440}{2200} = 1/5$ ].

Even with  $\beta' = 0$  a point of inflection can very well occur somewhere in the curve  $T = f(x)$ . The corresponding condition for the occurrence of a point of inflection at  $x = 0$  in the curve  $T = f(x')$  becomes:

$$\left(\frac{x}{x'}\right)_0 = \frac{q_1 + 4T_1}{q_1 + 4T_1 - 2(q_1 - q_2)} = \frac{1}{1 - 2 \frac{q_1 - q_2}{q_1 + 4T_1}}$$

or

$$\frac{q_2}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = - \log \left( 1 - 2 \frac{q_1 - q_2}{q_1 + 4T_1} \right),$$

for which we may write for small values of  $q_1 - q_2$ :

$$\frac{q_2}{2T_1T_2} (T_1 - T_2) = 2 \frac{q_1 - q_2}{q_1 + 4T_1}.$$

This is only possible when  $q_1 > q_2$ . Again we may write:

$$\frac{q_1 - q_2}{q_2} = \frac{(q_1 + 4T_1)(T_1 - T_2)}{4T_1T_2} = \left( 1 + \frac{q_1}{4T_1} \right) \left( \frac{T_1}{T_2} - 1 \right),$$

or

$$\frac{q_1}{q_2} = \frac{T_1}{T_2} + \frac{q_1}{4T_1} \left( \frac{T_1}{T_2} - 1 \right),$$

i. e.

$$\frac{q_1}{4T_1} = \frac{q_2}{T_1} \frac{T_1 - T_2}{T_2 - 1} \dots \dots \dots (15a)$$

If e.g.  $T_1 = 1100$ ,  $T_2 = 900$ ,  $q_1 = 2200$ ,  $q_2 = 1650$ , the first member is again  $1/2$ , and also the second member is  $\frac{1/3 - 11/3}{11/3 - 1} = 1/2$ .

[The term  $2 \frac{q_1 - q_2}{q_1 + 4T_1}$  is now  $\frac{1100}{6600} = \frac{1}{6}$ ].

Also in the curve  $T = f(x')$  a point of inflection may occur even with  $\beta' = 0$ .

And now we have given a complete answer to the question

raised in the beginning of § 3. The point of inflection at  $L$  (fig. 7) need not have disappeared in either of the two meltingpoint-curves, when  $\beta'$  has reached the extreme value 0.

In a following paper we shall give a fuller discussion of the important limiting case  $\beta' = 0$ .

4. Finally we wish to discuss more at length an important property of the *eutectic* point  $C$ , which was only shortly mentioned in the preceding communication. (i.e., p. 166).

A rule was namely given there of very general application, i. e. :

*When  $\alpha'_1 = \alpha'_2$  (i. e. latent heat required for the mixing of the first component with  $x = 1$  is equal to that of the second component with  $x = 0$ ) the compositions of the two solid phases will be complementary.*

We shall proceed to give the proof of this thesis.

Evidently the system of equations holds for the eutectic point (the compositions  $x'_1$  and  $x'_2$  of the solid phase are there in equilibrium with that of the liquid  $x$ ) :

$$T = \frac{T_1(1 - \beta' x_1'^2)}{1 + \frac{RT_1}{q_1} \log \frac{1 - x_1'}{1 - x}} = \frac{T_2 \left( 1 - \frac{q_1}{q_2} \beta' (1 - x_1')^2 \right)}{1 + \frac{RT_2}{q_2} \log \frac{x_1'}{x}} = \frac{T_1(1 - \beta' x_2'^2)}{1 + \frac{RT_1}{q_1} \log \frac{1 - x_2'}{1 - x}} = \frac{T_2 \left( 1 - \frac{q_1}{q_2} \beta' (1 - x_2')^2 \right)}{1 + \frac{RT_2}{q_2} \log \frac{x_2'}{x}} \dots \dots \dots (16)$$

If we solve from this  $\log(1-x)$  and  $\log x$ , we get :

$$\left. \begin{aligned} \log(1-x) &= \log(1-x'_1) + \frac{q_1}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) + \frac{q_1}{RT} \beta' x_1'^2 \\ \log x &= \log x'_1 + \frac{q_2}{R} \left( \frac{1}{T_2} - \frac{1}{T} \right) + \frac{q_1}{RT} \beta' (1-x'_1)^2 \\ \log(1-x) &= \log(1-x'_2) + \frac{q_1}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) + \frac{q_2}{RT} \beta' x_2'^2 \\ \log x &= \log x'_2 + \frac{q_2}{R} \left( \frac{1}{T_2} - \frac{1}{T} \right) + \frac{q_1}{RT} \beta' (1-x'_2)^2 \end{aligned} \right\}$$

from which follows by equalization :

$$\log \frac{1-x_1'}{1-x_2'} = \frac{q_1}{RT} \beta' (x_2'^2 - x_1'^2); \quad \log \frac{x_1'}{x_2'} = \frac{q_1}{RT} \beta' [(1-x_2')^2 - (1-x_1')^2],$$

which is evidently satisfied by

$$\underline{x_2' = 1 - x_1'}, \quad \dots \dots \dots (17)$$

q. e. d.

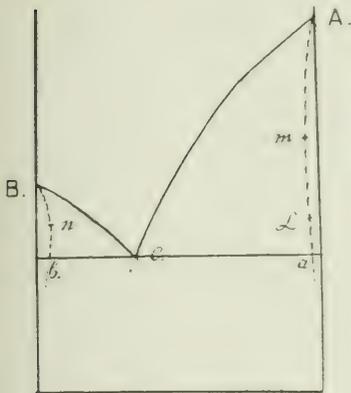


Fig. 1.

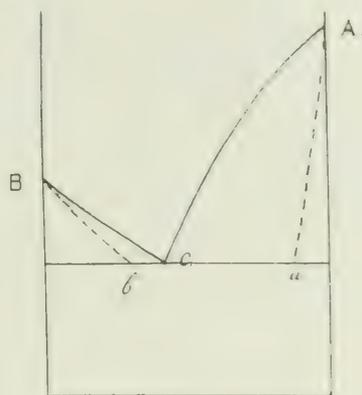


Fig. 2.

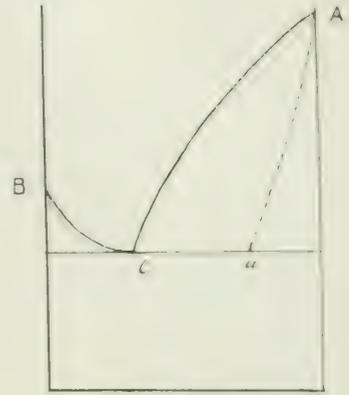


Fig. 3.

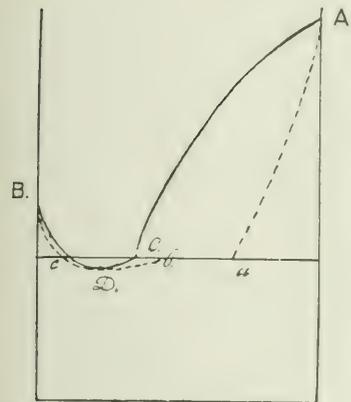


Fig. 4.

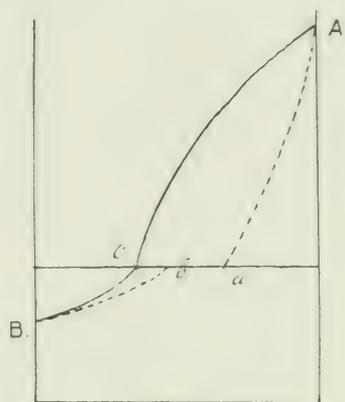


Fig. 5.

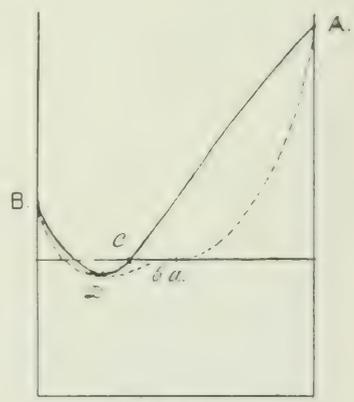


Fig. 6.

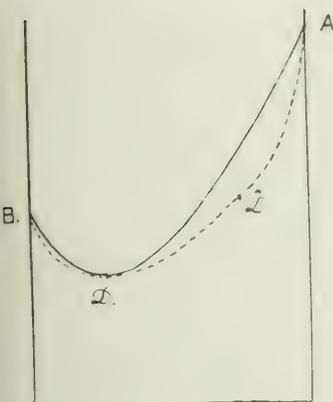


Fig. 7.

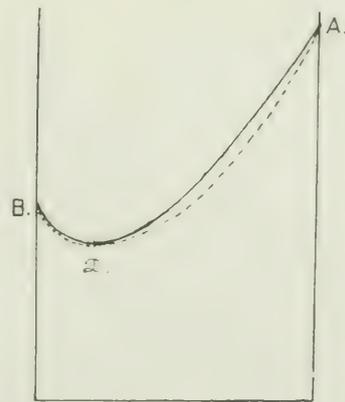


Fig. 8.

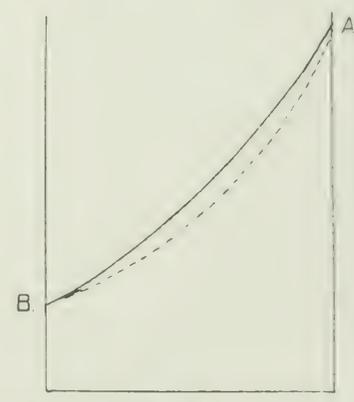


Fig. 9.



The two above equations pass now into one :

$$\log \frac{1-x_1'}{x_1'} = \frac{q_1}{RT_e} \beta'(1-2x_1') \dots \dots \dots (18)$$

In this complementary composition we have a distinct criterion, whether or no it is allowed to put  $x_1' = x_2'$  (i. e.  $r = 0$ ). Further the equation (18) furnishes a simple means, when  $r$  may really be put  $= 0$ , for calculating the quantity  $\beta'$  from the composition  $x_1'$  of the solid phase at the eutectic point.

If we find e.g.  $x_1' = 0,1$ , we may find by means of  $T_e = 500$ ,  $q_1 = 2400$  :

$$\log 9 = \frac{2400}{1000} \beta' \times 0,8,$$

hence :

$$\beta' = \frac{25}{48} \log 9 = 1,14.$$

If  $x'$  had been 0,01, we should have found with the same values of  $T_e$  and  $q_1$  :

$$\log 99 = \frac{12}{5} \beta' \times 0,98,$$

hence :

$$\beta' = \frac{125}{294} \log 99 = 1,95.$$

It is seen, that a slight increase of  $\beta'$  is able to depress the composition  $x_1'$  of the solid phase at the eutectic point very strongly. This is of course in connection with the enormously strong decrease of the relation  $\frac{x'}{x}$  with increasing  $\beta'$ . This relation was e.g. for  $T = T_1$

and great  $\beta'$  represented by  $\left(\frac{x'}{x}\right)_0 = e^{-\frac{\alpha'}{RT_1}}$  (see § 3), which converges very quickly to 0.

**Chemistry.** — “*The phenomena of solidification and transformation in the systems  $NH_4NO_3$ ,  $AgNO_3$  and  $KNO_3$ ,  $AgNO_3$ .*” By Professor H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of September 26, 1903.)

Of the nitrates of univalent metals, those of Li, Na, Ag,  $NH_4$ , K, Tl have been studied more in detail as to their mutual relations. It has already been shown that the nitrates of the first three are very prone to yield mixed crystals and the same takes place with the last three.  $LiNO_3$  and also  $NaNO_3$  do not seem to form with the

nitrates of the last group any mixed crystals at all or else only to a small extent and in any case they do not enter into chemical combination.

As regards the relation of  $\text{AgNO}_3$  to the nitrates of the second group, the only system examined up to the present (by VAN EYK) was that consisting of  $\text{AgNO}_3 + \text{TlNO}_3$  in which a compound in the proportion 1:1, was formed. To complete our knowledge in this direction, the systems  $\text{NH}_4\text{NO}_3 + \text{AgNO}_3$  and  $\text{KNO}_3 + \text{AgNO}_3$  have been investigated by ZAWIDZKI and USSOW and the results are comprised in the Figures 1 and 2.

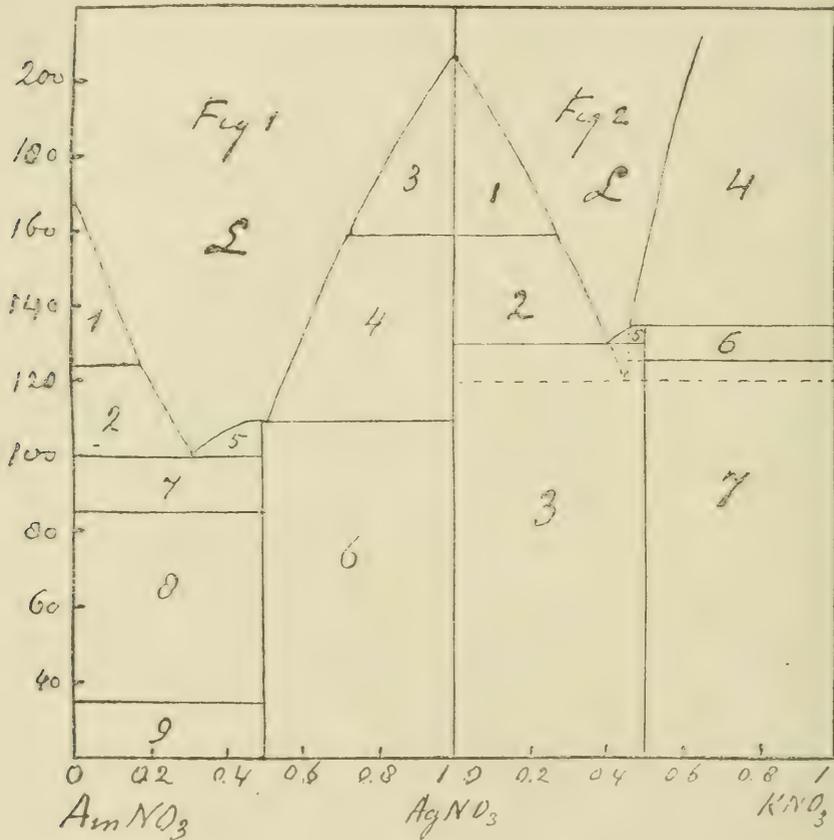


Fig. 1 and 2.

The first system is interesting on account of the fact that with  $\text{NH}_4\text{NO}_3$ , four and with  $\text{AgNO}_3$ , two solid phases succeed each other which, starting from the melting-point, we will designate by Am 1—4 and Ag 1—2.

It now appears that in the case of mixtures of the two salts the

transition point of  $\text{AgNO}_3$  and the first transition point of  $\text{NH}_4\text{NO}_3$  falls in the region where these mixtures are still partially liquid; the two lower transition points of  $\text{NH}_4\text{NO}_3$ , however, are situated in the region where everything has already become solidified.

Owing to this, the deposition of  $\text{AgNO}_3$  from melted mixtures rich in silver takes place according to two lines which meet each other at  $160^\circ$ ; the solidification of  $\text{NH}_4\text{NO}_3$  from mixtures rich in this salt, also takes place along two lines which meet each other at  $125^\circ$ . Neither transition point is modified by the mixing process, from which we may conclude that the salts are deposited in a pure condition and do not yield mixed crystals.

From the intermediate concentrations, however, a compound  $\text{D} = \text{NH}_4\text{NO}_3 \cdot \text{AgNO}_3$  is deposited with a pure melting point at  $109.6^\circ$ . Its melting-point-line extends towards the Ag-side only up to 52 Mol. %, towards the  $\text{NH}_4$ -side up to 30 % Ag. Consequently, all mixtures of 50—100 % Ag solidify at  $109.6$  to conglomerates of  $\text{D} + \text{Ag}_2$  and all mixtures of 0—50 % Ag at  $101.5$  to conglomerates of  $\text{Am}_2 + \text{D}$ .

The latter, on further cooling, undergo a new transformation at  $85^\circ$  and  $35^\circ$  owing to the reversion of  $\text{Am}_2$  into  $\text{Am}_3$  and then into  $\text{Am}_4$ . As both take place in the different mixtures at the same temperature at which reversion of the pure  $\text{AmNO}_3$  takes place, this proves that no mixed crystals occur between this salt and the double salt.

If now we express the liquid mixtures by L we have in Fig. 1 the following regions.

1	$\text{Am}_1 + \text{L}$	7	$\text{Am}_2 + \text{D}$	3	$\text{L} + \text{Ag}_1$
2	$\text{Am}_2 + \text{L}$	8	$\text{Am}_3 + \text{D}$	4	$\text{L} + \text{Ag}_2$
5	$\text{D} + \text{L}$	9	$\text{Am}_4 + \text{D}$	6	$\text{D} + \text{Ag}_2$

The system  $\text{AgNO}_3 + \text{KNO}_3$  is simpler in so far that  $\text{KNO}_3$  has only got one transition temperature at  $126^\circ$ .

The transition point of  $\text{AgNO}_3$  again falls within the partially liquid region and the solidification of the mixtures rich in Ag therefore, again takes place according to two lines which meet each other at  $160^\circ$ . Under normal conditions, the transition point of  $\text{KNO}_3$  falls within the solid region, consequently there is only one melting point line for the first form of the  $\text{KNO}_3 : \text{K}_1$ ; in the figure this line is represented only from  $210^\circ$  to lower temperatures; it must be imagined to extend to the  $\text{KNO}_3$  axis at its melting point of  $338^\circ$ .

From the intermediate concentrations there is also deposited a double salt  $\text{D} = \text{KNO}_3 \cdot \text{AgNO}_3$  but its melting-point-line only extends from

131° and 38 %  $\text{KNO}_3$  to 134°.5 and 45 %  $\text{KNO}_3$ .

Consequently, there exists no pure melting point but D is transformed on heating to 134°.5 into  $\text{KNO}_3$  solid + solution of 45 %.

All mixtures of 0—50  $\text{KNO}_3$  solidify at 131° to  $\text{Ag}_2 + \text{D}$ , all mixtures of 50—100  $\text{KNO}_3$  at 134°.5 to conglomerates of  $\text{D} + \text{K}_1$ . The first named remain unchanged on further cooling. The last named ought to change at 126° into  $\text{D} + \text{K}_2$  but this takes place with great difficulty.

The double salt is also not readily formed. If it does not make its appearance, the melting-point-line for  $\text{K}_1$  runs through to 126°, and below this  $\text{K}_1$  is converted into  $\text{K}_2$  much more readily than in the solid conglomerates. The melting-line of  $\text{K}_2$  runs through to 120° at 42 %  $\text{KNO}_3$  where it meets the prolongation of the melting line of  $\text{Ag}_2$ . If D does not appear, *all* liquid mixtures solidify at 120° to a conglomerate of  $\text{Ag}_2 + \text{K}_2$ .

The following zones comprised between the full lines represent stable conditions

1	$\text{Ag}_1 + \text{L}$	4	$\text{L} + \text{K}_1$
2	$\text{Ag}_2 + \text{L}$	5	$\text{L} + \text{D}$
3	$\text{Ag}_2 + \text{D}$	6	$\text{D} + \text{K}_1$
		7	$\text{D} + \text{K}_2$

All metastable boundaries are indicated by dotted lines. The regions concerned may be easily deduced from the figure.

From the above it follows that at the ordinary temperature, only the simple salts in the forms which are stable at that temperature and also the double salts 1:1 can occur as stable conditions; this agrees with what RETGERS has previously found for the products of crystallisation from aqueous solutions at 15°.

**Chemistry.** — “*The transformation of benzidine*”. By Prof. A. F. HOLLEMAN and J. POTTER VAN LOON.

(Communicated in the meeting of September 26, 1903).

In the report of the meeting of this section of Nov. 29, '02 there will be found a preliminary communication as to the experiments conducted in my laboratory by Dr. J. POTTER VAN LOON, who has since brought his research to a close. His results are briefly described below.

The method by which he succeeded in obtaining benzidine and hydrazobenzene in a perfectly pure condition has already been given in the preliminary communication. In connection with this it may be mentioned that hydrazobenzene was separated as a snow-white

substance, but after a few days exposure to the air it again turns faint yellow.

An improvement was also desirable in the quantitative determination of benzidine. At first VAN LOON collected the precipitated benzidine sulphate on a weighed filter, which was then dried at  $100^{\circ}$  in a steam oven and reweighed. Here we met with the unpleasant fact that the filter often turned blackish probably owing to a decomposition of the sulphate, which may unfavourably affect the determinations. The improved process now consisted in removing the washed sulphate from the filter and boiling it with excess of standard alkali. If now the excess of alkali is titrated at the boiling heat with standard acid, the benzidine sulphate behaves like free sulphuric acid when litmus is used as indicator. In this way the determination becomes more rapid and accurate. The usual correction for the solubility of benzidine sulphate had, of course, to be made.

The determinations made by Dr. VAN LOON of the ratio between the quantities of benzidine and diphenylene formed during the transformation of hydrazobenzene by acids have demonstrated the influence of various circumstances on that relation and may be best represented in a tabular and graphical form.

I. INFLUENCE OF THE CONCENTRATION OF THE ACID (HYDROCHLORIC ACID).

a) Solvent: Water.

Temp.  $18^{\circ}$ — $25^{\circ}$ .

Concentration of the acid.	Amount of acid in mgr. mol.	Mgr. mol. hydrazobenzol.	% benzidine.	Weight of diphenylene on 100 parts of benzidine.
25% = 7.8 n.	77.8	1 —	84.5	18.3
25% = 7.8 n.	77.8	2.014	80.0	25
3.90 n.	77.8	2.—	90.0	11.1
$\frac{1}{1}$ n.	50	2.—	90.5—89.5	10.5—12.4

b) Solvent: Alcohol of 50%<sup>1)</sup>.

Temp.  $25^{\circ}$ .

Concentration of the acid.	Amount of acid in mgr. mol.	Mgr. mol. hydrazobenzol.	% benzidine.	Weight of diphenylene on 100 parts of benzidine.
3.1 n.	77.8	2.—	80.0	25
$\frac{1}{1}$ n.	50.—	2.—	84.8	17.9
0.6 n.	30 —	1.440	83.6	19.6
0.1 n.	5.—	2.—	83.0	20.5

1) Always percents of weight are meant.

## II. INFLUENCE OF THE SOLVENT. Temp. 18°—25°. HYDROCHLORIC ACID.

Nature of the solvent.	Concentr. of the acid	Amount of acid in mgr. mol	Mgr. mol hydrazo.	% benzidine.	Weight of diphenyline on 100 parts of benzidine.
Alcohol of 97%	0.12 n.	12	1.533	80.5	24.2
» » 50%	0.1 n.	10 and 5	1.6304 and 2	84.1 and 83.1	18.9—20.3
» » 50%	1/1 n.	50	2	84.8	17.9
» » 15%	0.1 n.	5	2	87.5	14.3
Water	1/1 n.	50	1.6304 and 2	90.5 and 89.0	10.5—12.4
Methyl alcohol	0.1 n.	5	2	74 %	35.1

Alcohol and methyl alcohol alter the relation of the transformation to the disadvantage of the benzidine and the effect becomes greater when the amount of water becomes less. This may be caused by the circumstance that in another medium the reaction may take a different course (for instance, the velocity of the formation of diphenyline may increase) but it is also possible that the deviation must simply be attributed to the increased solvent action which dilute alcohol exerts on hydrazobenzene or an intermediary product of the reaction. It is *not* due to an increased solubility of benzidine sulphate in dilute alcohol as has been proved by a purposely made direct experiment.

## III. INFLUENCE OF THE KIND OF ACID.

a) Temp. 100°. Water.

Acid.	Concentration.	Amount of acid in mgr. mol.	Mgr. mol. hydrazobenzene	% benzidine.
HCl	0.03 n.	4	1.6304	66.4—70.6
HNO <sub>3</sub>	0.05 n.	6.4	1.6304	67.3—71.7
H <sub>2</sub> SO <sub>4</sub>	0.03 n.	4.4	1.6304	63.1
HBr	0.03 n.	4	1.6304	65.8

As at 100° a small quantity of azobenzene or aniline may be formed (the formation of the latter has not been investigated for the weak hydrochloric acid concentration) the figures for the formation of diphenyline would be valueless and they have, therefore, been omitted in table III. Those for benzidine are probably a little too low as the formation of azobenzene could not be entirely avoided.

b) Temp. 25°. 50 % Alcohol. Columns as under I and II.						
HCl.	1/1 n.	50	2	84.8	17.9	
HNO <sub>3</sub> .	1/1 n.	50	2	82.2	21.7	
H <sub>2</sub> SO <sub>4</sub> .	1/1 n.	50	2	89.8	41.4	
CHCl <sub>2</sub> .COOH.	1/1 n.	50	2	83.5	49.8	

Except for sulphuric acid which yields a higher value, the relation of the transformation does not differ much in the case of the other acids.

## IV. INFLUENCE OF THE TEMPERATURE.

a) Alcohol of 50% Hydrochloric acid.

Temp.	Conc. of the acid.	Amount of acid in mgr. mol.	Mgr. mol. hydrazo.	% benzidine.	Weight of diphenyl-ine on 100 parts of benzidine.
0°	0.1 n.	5	1	87.8	43.9
25°	1/1 n.	50	2	84.8	17.9
50°	1/1 n.	50	2	79.0	26.6
75°	1/1 n.	50	2	67.4	48.4
b) Water. Hydrochloric acid.					
48°	1/1 n.	50	1.6304	90.5	10.5
25°	1/1 n.	50	2	89.0	12.4
50°	1/1 n.	50	2	86.6	15.5
75°	1/1 n.	50	2	80.8	23.8
100°	1/1 n.	50	2	74.9	33.51
160°	0.03 n.	4	1.6304	66.4—70.6	50.6—41.6

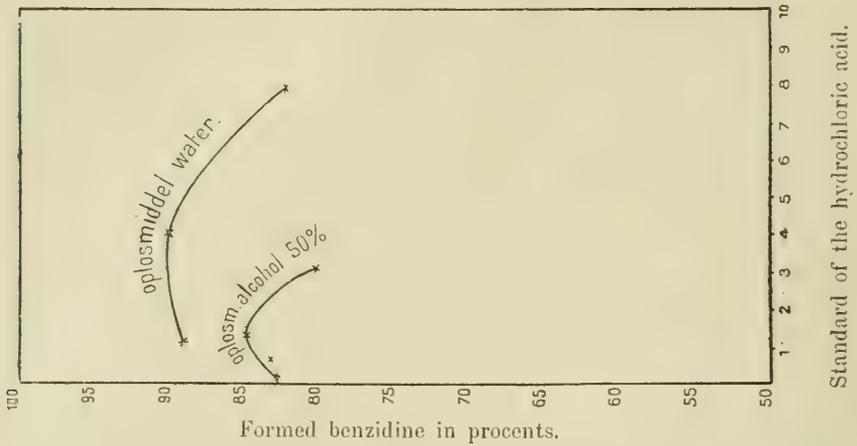
The figures given in the tables are in most cases the average of several fairly concordant determinations.

The influence of the temperature as shown by this table is again the same for both solvents and is shown by a fall in the ratio of the transformation with a rise in the temperature.

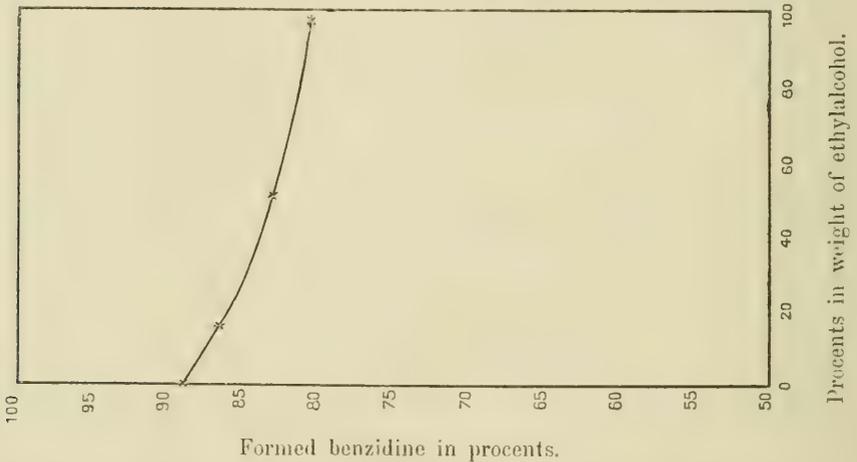
The following observation should be made as to the last column contained in these tables; the substance which was not precipitated as benzidine sulphate is supposed to have been converted into diphenyl-ine. This, however, has only been once isolated as such, so that it is not impossible that other bases besides diphenyl-ine may have been formed, the sulphates of which are soluble in water. As other investigators have already taken up this subject, Dr. VAN LOON has not extended his research in that direction.

The graphic representations, following here, are those of the above mentioned tables.

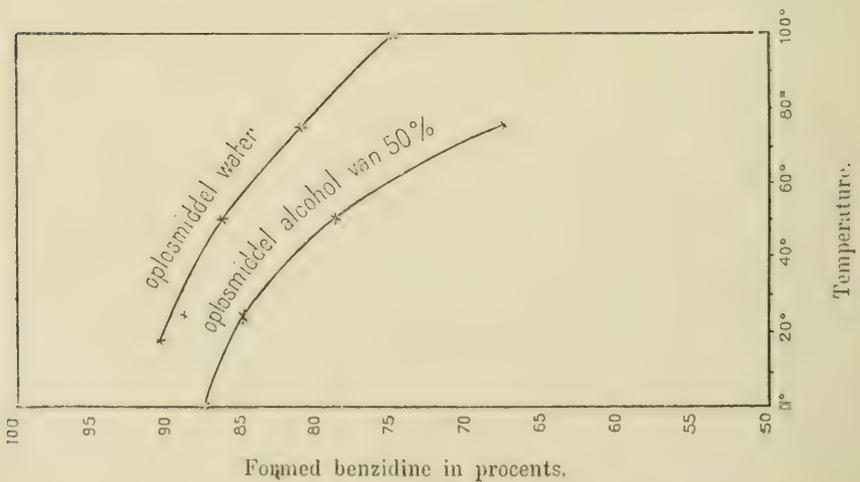
Fig. I. Influence of the concentration of the acid on the ratio of transformation.  
Temp. 25°.



Figur II. Influence of the amount of alcohol on the ratio of transformation.  
0.1 n. hydrochloric acid,  $t = 25^\circ$ .



Figur III. Influence of the temperature on the ratio of transformation.  
1. — n. hydrochloric acid



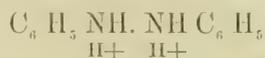
Dr. VAN LOON has also been engaged in determining the velocity of the transformation. An excess of finely powdered hydrazobenzene was introduced into dilute alcohol, to which had been added acid of a definite concentration, the mixture being vigorously stirred. At stated times certain quantities of liquid were withdrawn from the mixture and the amount of benzidine was quantitatively determined.

If  $C_b$  is called the concentration of the benzidine formed,  $C_{HCl}$  that of the hydrochloric acid at any moment, the equation

$$\frac{d C_b}{dt} = K C_{HCl}^2$$

was found to represent the transformation; in this  $t$  is the time (in minutes) and  $K$  the reaction constant. No special figure is given for the concentration of the hydrazobenzene as this may be taken as constant in the modus operandi followed.

The transformation is due to the hydrogen ions of the acid, for on comparing the action of hydrochloric acid and dichloroacetic acid the reaction constant was shown to be proportional to the degree of ionisation of the acids employed. This caused Dr. VAN LOON to suggest that during the transformation two H-ions are first linked to hydrazobenzene forming



and that then the repulsion of the two positive charges causes the molecule to break up between the two nitrogen atoms, whereupon the two portions again unite in such a manner that the positive charges are at a greater distance from each other. This representation accounts for the presence of  $C_{HCl}^2$  in the equation of velocity, as according to this equation one mol. of hydrazobenzene reacts with two H-ions.

Chem. Lab. Univ. Groningen, July 1903.

**Chemistry.** — “*The transformation of diphenylnitrosamine into p-nitroso-diphenylamine and its velocity.*” By H. RAKEN. (Communicated by Prof. C. A. LOBRY DE BRUYN as communication N<sup>o</sup>. 6 on intramolecular rearrangements).

(Communicated in the meeting of September 26, 1903).

In 1886 OTTO FISCHER discovered the interesting fact that under the influence of alcoholic hydrochloric acid the nitrogen-combined nitrosogroup of methylphenylnitrosamine changes place with the para-hydrogen atom of the benzene nucleus and is thus converted into the isomeric nitrosobase.



FISCHER and ED. HEPP have made a closer study of this reaction and found it to be a general one<sup>1)</sup>; it also takes place with diphenylnitrosamine.

It was deemed of importance to study the exact conditions under which this transformation takes place and particularly to learn its order by means of a determination of the reaction velocity. A method which permitted the quantitative estimation of the two isomers in presence of each other with sufficient accuracy, was not at hand. The chemical behaviour of the two isomers does not differ greatly and the nitrosobase (at least in this case) is far too weak to be titrated. It was therefore attempted to utilise the difference in colour of the two isomers; diphenylnitrosamine has a faint yellow colour, which in dilute solutions may be neglected. The nitrosobase however, in combination with hydrochloric acid forms a brown powder whose dilute alcoholic solution is deep yellow, whilst more concentrated solutions are dark brown or red.

It was therefore decided to carry out the measurements by means of a colorimetric process using the polarisation-colorimeter of Krüss. An unexpected difficulty arose, however, owing to the fact that different preparations of the hydrochloride gave greatly different results when examined in the colorimeter, although they had been prepared in exactly the same manner. As it was, of course, necessary to prepare the standard liquids with the perfectly pure salt, I have taken a great deal of trouble to obtain this. It appeared that a solution of this salt is slightly decomposed and darkened by the oxygen of the air and by prolonged contact with excess of hydrochloric acid; the salt was therefore prepared in an atmosphere of carbonic acid and under specified conditions. The compound was taken as pure when different preparations gave the same result in the colorimeter; an analysis was of no service. And after it had been found that the free base (which in the solid state forms steel-blue needles) exhibits the same colour as the hydrochloride in dilute alcoholic solutions, the basis of the measurements was obtained.

From the colorimetric identity of the free base and the hydrochloride it follows that the latter, in very dilute solutions, must be completely alcoholically dissociated and also that only solutions of a certain degree of dilution are comparable with each other.

<sup>1)</sup> Ber. 19. 2991. 20. 1247. 2471. 21. 861. Ann. 255. 144. (1886—1889) etc.

The concordant and very definite results obtained during the measurements may in turn be taken as a proof that the standard-comparison solutions were trustworthy.

Experiments were made in alcoholic solution with hydrochloric acid as catalyzer.

The results are briefly as follows:

1. The reaction is one of the first order.

2. The reaction constant is proportional to the concentration of the hydrochloric acid causing the transformation. In absolute ethyl alcohol at  $35^{\circ}$  (time in hours) was found for

1 mol. HCl	2 mols. HCl	3 mols. HCl
$k = 0.0081$	0.018	0.026

3. Addition of water causes a serious fall in the reaction constant; for instance, for  $t = 35^{\circ}$  and 3 mols. HCl in abs. alcohol:

$$k = 0.026; \text{ in } 92.5\% \text{ alcohol: } k = 0.0026.$$

The water apparently withdraws a portion of the hydrochloric acid or renders it less active.

4. The temperature coefficient is very great; about 5 for each  $10^{\circ}$ .

We may therefore draw the general conclusion that the transformation of the nitrosamines into the nitrosobases is a real intramolecular displacement of atoms. This is all the more likely if we consider that in this case the velocity with which the transformation product was formed, was measured. This result remains the same if we suppose that at first (with unmeasurably large velocity) an intermediate additive product was formed from the nitrosamine and the hydrochloric acid acting as catalyzer. We then have, practically, measured the transformation of the latter into the isomer; that transformation however requires also an intramolecular rearrangement.

We shall later on return to the possibility of the occurrence of an intermediate product. Further particulars will then be communicated as to the action of other catalyzers and on the influence of other solvents on the migration; experiments in this direction are already in progress.

**Physics.** — *“The periodicity of solar phenomena and the corresponding periodicity in the variations of meteorological and earth-magnetic elements, explained by the dispersion of light.”*  
By Prof. W. H. JULIUS.

(Communicated in the meeting of September 26, 1903).

Table of contents.

Introduction.

- I. The path of the projection of the Earth on the Sun. The probable origin of the 11-year period.
- II. The variability of the solar radiation.
- III. The periodical variations in the appearance of the Sun.
  1. Sun-spots and faculae.
  2. Prominences.
- IV. The periodicity in the variations of meteorological and earth-magnetic elements.
  1. Do these phenomena require the hypothesis that the Sun exhibits a varying activity?
  2. Effects of the movement of the Earth through the irregular field of the Sun's radiation.
    - A. The semi-annual and annual periods in the position of the Earth in the irregular field of radiation.
    - B. The periodicity of the fluctuations of illumination which coincides with the periodicity of solar phenomena.
  3. Polar lights.
  4. The annual variation in the diurnal inequality of terrestrial magnetism.
  5. Magnetic disturbances.
  6. The annual variation in the daily oscillations of atmospheric pressure.
  7. The annual and secular variations of atmospheric pressure.
  8. Cosmic influence on other terrestrial phenomena.

Summary of results.

INTRODUCTION.

The whole science of astrophysics rests on the hypothesis that the same laws, which we have recognized by observation and experimental research, hold good for other celestial bodies as well as for the Earth, and that we are justified in applying to the Sun and the comets, to nebulae and double stars, the results of thermodynamics, of spectrum-analysis, of the theory of electrons. It would therefore be illogical to make an exception with regard to our knowledge of the refraction and dispersion of light in masses of variable optical density; and by adhering to the supposition, that in the Sun and its nearest vicinity the light travels in straight lines, we should take an untenable standpoint.

The results of some recent investigations <sup>1)</sup> all tend to confirm the hypothesis that the causation of anomalous dispersion is a general property of matter. Thence, even highly rarefied gases, whose density is unequally distributed, cause some kinds of rays to be considerably deflected. All the conclusions arrived at by YOUNG, LOCKYER and others, as to the thickness of the various concentric layers in the solar atmosphere, the velocities of the prominences, the displacement of matter in the sun-spots, the dissociation of elements in the Sun etc., must be sacrificed in so far as they are based on the erroneous notion that the objects are situated in the exact direction where they are seen by us.

A. SCHMIDT <sup>2)</sup> has gone so far as to demonstrate that the sharply defined circular outline of the Sun's disc is no proof of the Sun being a spherical body. Owing to the curvilinear propagation of the rays, a gradually fading luminous mass of gas might appear to us as a sharply outlined disc.

We may therefore be allowed to consider the Sun an unconfined gaseous mass.

By taking also into account the laws of the anomalous dispersion of light, we succeeded in finding explanations for almost all the phenomena observed on the surface of the Sun and on its edge <sup>3)</sup>. We felt justified in starting from the simple supposition that in the gaseous, unlimited body of the Sun, the several elements are not locally separated but intrinsically mixed. Perhaps future investigations may lead us to admit that in the solar body some elements are locally separated, but I think that the present state of our knowledge regarding the properties of sun-spots, faculae and prominences does not warrant such an assumption.

Our new conception of the Sun leaving no longer any room for the hypothesis of a periodical activity manifesting itself in violent eruptions, we are naturally led to inquire whether all the phenomena attributed to this cause, may equally well — perhaps better — be explained as effects of the dispersion of light.

The following data may assist in the elucidation of this question.

<sup>1)</sup> O. LUMMER und E. PRINGSHEIM, Zur anomalen Dispersion der Gase, *Physik. Zeitschr.* 4, S. 430—431. 1903.

H. EBERT, Die anomale Dispersion der Metaldämpfe. *Phys. Zeitschr.* 4, S. 473—476.

H. EBERT, Die anomale Dispersion und die Sonnenphänomene, *Astr. Nachr.* 162, S. 194—195.

<sup>2)</sup> A. SCHMIDT, Die Strahlenbrechung auf der Sonne. Stuttgart, 1891.

<sup>3)</sup> W. H. JULIUS, *Proc. Roy. Acad. Amst.* II, p. 575—588; III, p. 195—203; IV, p. 162—171; 589—602; 662—666.

I. THE PATH OF THE EARTH'S PROJECTION ON THE SUN.  
THE PROBABLE ORIGIN OF THE 11-YEAR PERIOD.

If it be true that sun-spots, faculae and prominences are effects of ray-curving, it stands to reason that their form and situation will depend in a far greater measure on the position occupied by the observer, than would be the case, if they were themselves light-emitting bodies.

A correct idea of the movement of the Earth with respect to the revolving body of the Sun must therefore be the basis of our investigations. Unfortunately it is impossible to give an absolutely exact idea of this relative motion, for not only are we in ignorance of the exact period of the Sun's rotation, but it is extremely difficult to define the meaning of that term, because we take the Sun to be a mobile gaseous mass. On the other hand it is quite evident that we are dealing with a periodical phenomenon; the only question therefore is, whether we shall succeed in selecting from the various values on record, the one which has the greatest significance from our point of view on Earth.

As a matter of course we select a synodical period of revolution. It is a known fact that different values for the period are obtained from the movement of spots and faculae, varying from 26 to 30 days according to their heliographic latitude. By the application of DOPPLER'S principle, DUNÉR found that near the equator, the period of rotation of the photosphere was 25,46 days and at 75° latitude up to 38,55 days. In 1871 HORNSTEIN observed in the deviations of the magnetic declination at Prague a period of about 26 days, which other investigators have found also in various meteorological phenomena. The results obtained led to the conclusion, that the rotation of the equatorial regions of the Sun exercises a greater influence on the Earth than that of the other zones.

From the following table it will appear how indefinite as yet is our knowledge of the period of the Sun's rotation :

STRATONOFF (faculae near the equator)	26,06 <sup>1)</sup>
CARRINGTON (sun-spots near the equator)	26,82 <sup>1)</sup>
DUNÉR (photosphere near the equator)	25,46 <sup>2)</sup>
HORNSTEIN (magnetic observations at Prague)	26,5 <sup>1)</sup>
AD. SCHMIDT (most probable value deduced from the mag-	

<sup>1)</sup> ARRHENIUS, Lehrb. d. kosmischen Physik, p. 148.

<sup>2)</sup> This value is communicated by DUNÉR as being the sidereal period of rotation, and appears to have been generally accepted as such. Prof. J. C. KAPTEYN, however, kindly informed me that in DUNÉR'S interpretation an error has slipped, and that he result must be taken as the synodical period.

netic observations of BROUX, HORNSTEIN, MÜLLER and LIZNAR, until 1886)	25,92 <sup>1)</sup>
AD. SCHMIDT (magnetic observations at Batavia)	25,87 <sup>1)</sup>
VAN DER STOK (barometrical observations at Batavia and St. Petersburg and magnetic observations at Prague and St. Petersburg)	25,80 <sup>1)</sup>
VON BEZOLD (thunderstorms in S. Germany)	25,84 <sup>1)</sup>
EKHOLM and ARRHENIUS (polar lights)	25,929 <sup>2)</sup>
BIGELOW (meteorological and magnetic observations in the United States of America)	26,68 <sup>1)</sup>

The justification of the choice we make between these different numbers must for the greater part be found in the value of the consequences we derive from it. However, there are some good reasons why we should prefer a priori the value obtained from investigations on the frequency of polar lights by EKHOLM and ARRHENIUS. For although the results of others (especially those of AD. SCHMIDT and of VAN DER STOK), from a point of view of careful and critical reasoning, are of no less value than those of EKHOLM and ARRHENIUS, the variations of the barometer and the oscillations of terrestrial magnetism are phenomena of a more complicated nature than polar lights. They are influenced by local conditions, the distribution of land and water, etc.; because they partly depend on the circulation in the lower layers of the atmosphere. On the other hand it would appear that the polar lights take their origin principally in the higher layers and thus, by revealing to us more directly the action of the Sun's radiation, they will probably lead to a sharper determination of the period.

Whilst the periods of rotation necessarily differ in the various parts of the Sun's mass, there must be somewhere in the plane of the equator a series of points, where the synodical period of rotation is 25,929 days. Through these points we imagine a sphere *B*, the centre of which is laid in the centre of the Sun, and we make the sphere rotate around the Sun's axis with a constant angular velocity, so as to bring its synodical period of rotation at circa 25,929 days. This sphere represents to us "the rotating Sun", but we must keep in mind that with respect to *B* the various parts of the gaseous mass may alter their position.

<sup>1)</sup> AD. SCHMIDT, Sitz. Ber. Kais. Akad. d. W. Wien, Bd. 96, p. 990 and 1005.

<sup>2)</sup> VAN DER STOK, Verh. Kon. Akad. v. W. Amsterdam, 1890.

<sup>3)</sup> ARRHENIUS, Lehrb. d. kosmischen Physik, p. 148.

<sup>4)</sup> BIGELOW, Un. States Weather Bureau Bulletin No. 21, Washington, 1898. See also SCHUSTER's criticism, Terrestrial Magnetism III, p. 179.

The line  $AZ$ , which connects the centre  $A$  of the Earth with the centre  $Z$  of the Sun, intersects  $B$  at the point  $P$ . We call this point "the projection of the Earth on the Sun" and will determine its track on  $B$ .

The inclination of the Sun's equator on the ecliptic is  $7^{\circ}15'$ . About the 4<sup>th</sup> of June and the 6<sup>th</sup> of December the Earth passes through the nodal line.

Fig. 1 represents part of the sphere  $B$ ;  $EE'$  is the intersection

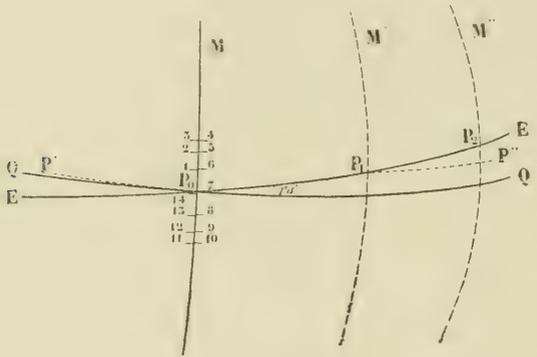


Fig. 1.

with the ecliptic,  $QQ'$  that with the Sun's equator. On the 4<sup>th</sup> of June the Earth's projection is in  $P_0$ . Through this point we draw the first meridian  $M$ . In the space of about 25,929 days  $M$  has made a synodical revolution and is intersected for the second time by the line  $AZ$  (not marked in the diagram) but this time at the point  $P_1$ , a little to the north of the equator. In the interval  $P$  has been describing one convolution  $P_0 P' P'' P_1$  of its helical course.

The next points of intersection  $P_2$  and  $P_3$  of the path of  $P$  with the first meridian again lie somewhat more to the north, but about the 4<sup>th</sup> of September the path has reached its utmost latitude  $7^{\circ}15'$  and then gradually descends towards the equator, which on the 6<sup>th</sup> of December it intersects a little beyond  $P_7$ .

All the points of intersection for one year are marked on the meridian  $M$  in its first position.  $P_8$  to  $P_{14}$  lie in the southern hemisphere.  $P_{14}$  is reached after  $14 \times 25,929 = 363,006$  days; the sidereal year has 365,256 days, consequently  $P_{14}$  does *not* coincide with  $P_0$ ; the track of  $P$  intersects the Sun's equator 2,25 days later.

During the second year,  $P$ , in its helical course, passes through entirely different points of our spherical surface than in the first year, and so do the successive annual spirals; they each time skip an angle

of  $\frac{2,25}{25,929} \times 2 \pi$ . The spirals of the twelfth and thirteenth year come again very close to that of the first year and lie on each side of it. It is therefore reasonable to expect that after a period of a little more than 11 years a very similar succession of incidents will take place. <sup>1)</sup>

It now remains for us to consider which conditions and phenomena may be governed by the position of  $P$  on the sphere.

The Sun is an immense mass of matter, and considering its age we may take it for granted, that within the memory of man it has remained in an almost stationary condition. We know that the violent eruptions which have been thought to take place on its surface, have led to a quite different conception, but at present we can realise <sup>2)</sup> that relatively small local variations in density, such as necessarily must occur in vortices along the surfaces of discontinuity between stationarily streaming layers of gas, are quite sufficient to produce strongly marked variable optical effects, such as prominences etc.

The large currents of the general solar circulation must be cyclic movements, which do not perceptibly alter the configuration of the entire mass, only causing along the surfaces of discontinuity a somewhat varying distribution of matter, due to undulations and whirling. We admit that on account of the Sun not being perfectly symmetrical around its axis, the movability of the parts involves a gradual change of form, but this change we will leave for the present out of consideration.

The rays emanating from the intensely bright core of the Sun reach us, whatever be the position of the Earth, through a space in which matter is unequally distributed.  $P$  therefore determines the principal characteristics of what might be called the "optical system" through which we see the Sun. When  $P$  shifts its position, this system changes with it; when  $P$  for the second time traverses the same path on the rotating sphere, to the eye of the observer on Earth all the phenomena which are produced by the refraction of light in the gases of the Sun, will repeat themselves in the same order.

<sup>1)</sup> Had we for the Hornstein period taken 25,924 days, instead of 25,929, then the mean value of the spot period would have been  $\frac{25,924}{2,32} = 11.17$  years. If therefore we wished to supplement the table on p. 272—273 with a value derived by theoretical considerations from the 11-year period, the number 25,924 would commend itself.

<sup>2)</sup> W. H. JULIUS, Proc. Roy. Acad. Amst. IV, p. 162—171.

## II. THE VARIABILITY OF THE SOLAR RADIATION.

It is well known that the composition as well as the intensity of the Sun's radiation is inconstant. As to the variation of the total intensity, this could not be ascertained by actinometrical measurement, owing to the capricious disturbances caused by the clouds; it has therefore been determined in an indirect way, from the values of the mean temperature all over the Earth. But the variability in the composition of the light has been revealed by a careful study of the FRAUNHOFER lines which has shown that several lines are at one time more enhanced than at others (JEWELL<sup>1</sup>) HALE<sup>2</sup>), LANGLEY<sup>3</sup>). In the spectrum of sun-spots also, in which several lines are comparatively very wide, N. LOCKYER<sup>4</sup>) noticed that the mean type of the spot-spectrum undergoes a periodical modification, the period of which coincides with that of sun-spot frequency.

As yet we have no certain indications that this periodicity also exists in the varying aspects of the FRAUNHOFER lines of the average photosphere spectrum. The abnormal spectrum photographed by HALE<sup>5</sup>) in 1894 (i.e. at a sun-spot maximum) presented, as has been shown elsewhere<sup>6</sup>), this peculiarity that the lines, which in the chromosphere spectrum are generally strongly marked (principally belonging to *Fe*, *H*, *Cu*, *Sr*, *Al*, *Ti*), were very faint, whilst the strong lines (belonging to *Zr*, *Mn*, *Y*, *V* and some of unknown origin) did not correspond to any of the chromospheric lines.

The periodical variability observed by LOCKYER in the spot spectrum consisted herein, that when at spot maximum the most enhanced lines were selected, they proved for the greater part to be "unknown lines" i.e. lines which in the normal solar spectrum are extremely weak, and that the strong lines of *Fe*, *Ni*, *Ti*, which during minima of spot periods often appear very wide, were then scarcely visible.

<sup>1</sup>) JEWELL, *Astroph. Journ.* 3, 89—113, 1896; 11, 234—240, 1900.

<sup>2</sup>) HALE, *Astroph. Journ.* 3, 156—161, 1896; 16, 220—233, 1902.

<sup>3</sup>) LANGLEY, *Annals of the Astroph. Observatory of the Smiths. Instit.*, Vol. I, 1900. On p. 208, 209 and 216 mention is made of irregular changes in the heat spectrum (especially in  $\phi$ ,  $\psi$  and  $\omega$ ), which do not seem to be occasioned by absorption in our atmosphere and are therefore the effect of cosmic influences. LANGLEY's excellent method of investigation may prove of the utmost value in the study of the variability of the Sun's radiation, as it gives directly comparable values for the energy of the various kinds of rays in this important part of the spectrum.

<sup>4</sup>) LOCKYER, *Proc. Roy. Soc.* 40, p. 347; 42, p. 37; 46, p. 385; 57, p. 199; 67, p. 409, (1886—1900).

<sup>5</sup>) HALE, *Astroph. Journ.* 16, 220—233.

<sup>6</sup>) W. H. JULIUS, *Proc. Roy. Acad. Amst.*, IV, 589—602.

The analogy between these abnormal appearances and those of the spectrum of HALE is obvious. Unfortunately the part of the spectrum investigated by LOCKYER (extending from  $\lambda 4863$  to  $\lambda 5893$ ) lies entirely outside the part photographed by HALE ( $\lambda 3812$ — $\lambda 4132$ ) which renders direct comparison impossible, but the parallelism to which we pointed, makes us anticipate that also in the aspect of the average photosphere spectrum, as well as in the spot spectrum, the 11-year period will be found.

LOCKYER holds that in years of spot maximum the Sun's activity is greatly increased; that the more violent eruptions then cause a considerable rise in its temperature. To this fact he ascribes the appearance of "unknown lines" and the weakening of the known lines, on the same principle as that which governs the variations produced in the emission spectra when passing from the arc to the induction spark<sup>1</sup>).

On the other hand CH. NORDMANN<sup>2</sup>) has published the results of an exhaustive inquiry into the variations of the temperature all over the Earth, between the years 1870 and 1900. From his statements it appears that the mean temperature undergoes indeed a periodical variation coinciding with the sun-spot period, but in this manner, that the maxima of the curve of spot frequency correspond to the minima of the temperature curve. This result seems to us a serious objection to the views of LOCKYER.

We will now see if by applying our theory, based on the dispersion of light, it is possible to find a consistent explanation for the results both of LOCKYER and NORDMANN.

To us the peculiarities of LOCKYER's spot spectrum are phenomena of the same nature as those observed in the abnormal spectrum described by HALE. We have found an explanation for the latter by supposing that just at the time when the photograph was taken, a long corona streamer was directed to the Earth, so that the line of sight almost coincided with the tangent of a surface of discontinuity. The visible structure of the corona with its long, almost straight lines, is to us an indication that the light of the Sun, according to the position occupied by the Earth, must at one time reach us along sharply defined surfaces of discontinuity and at others not. Provisionally neglecting possible variations in the distribution of matter which might take place in the Sun itself, the condition for each successive moment will be accurately defined by the place

<sup>1</sup>) LOCKYER, Proc. Roy. Soc. 67, p. 411—416, (1900).

<sup>2</sup>) CH. NORDMANN, C. R. 136, p. 1047—1050, (1903).

occupied by  $P$  in its helical course on the sphere, and we need only admit that at sun-spot maximum the separate rays of the total beam of light reaching the Earth, and from which  $PA$  is the central line, more often pass for a considerable distance closely along surfaces of discontinuity, than in times of minimum. If we admit this view, then our explanation of the spectral peculiarities reads thus:

A monochromatic beam of light, passing on its way closely along a surface of discontinuity, will undergo a marked change of divergency, when, for those particular waves, the medium has a great (positive or negative) refraction constant. We may rather expect an increase than a decrease of the divergency, because the medium becomes more rarefied with the increasing distance from the Sun's centre. As a rule such a beam will reach the Earth with a lesser intensity than the beams of rays which undergo less refraction. The consequence is that, through the scattering of neighbouring rays, all FRAUNHOFER lines which cause anomalous dispersion will have a somewhat darkened background. With some lines this background is broad ( $H, K$ , the lines of hydrogen, iron, in a word, all the well known widened lines of the solar spectrum); with others it is narrow; it depends on the proportion of these elements contained in the solar atmosphere and on the shape of the dispersion curve; but at all events, the mean intensity over the entire spectrum must have become less, by the light passing along the surfaces of discontinuity. In years of sun-spot maxima this happens more often than at minima, and this gives us the explanation of the results obtained by NORDMANN.<sup>1)</sup>

It now remains for us to prove that the same cause, which in the period of spot maximum makes weak lines in the spot spectrum to appear strengthened, makes also strong lines to appear weakened.

We again refer to our explanation of the abnormal spectrum of HALE. At that time we supposed the structure of the corona to be "tubular". Later considerations have induced us to define the structure of the exterior parts of the Sun as rather "lamellar", a correction

1) The kinds of rays which by dispersion have disappeared from the sunlight visible to us, travel to other parts of the universe, far from the orbits of the planets, where they would be seen as faculae, chromosphere light and corona light. If it were possible, by means of the spectroscope there to study the mean radiation, we should find in the continuous spectrum some bright lines, lying on both sides of the real absorption lines and in close proximity to them. Some stars present this phenomenon. It may, therefore, be explained by the assumption that they are bodies resembling the Sun, but that our line of sight forms a rather large angle with their equator.

which does not affect the arguments of our former conclusions. When the light travels through this structure almost parallel to the surfaces of discontinuity, the most strongly refracted rays follow undulating paths (vide Proc. Roy. Acad. Amst. IV, p. 596—597). They are kept together, are so to speak guided along the lamellar structure, and their intensity when reaching the Earth is greater than that of rays which undergo a lesser refraction. Consequently in the FRAUNHOFER lines which show a broad background (being produced by elements which are rather strongly represented in the coronal gases and which therefore, even during the minima of spot periods, give rise to marked anomalous dispersion) the parts nearest to the true absorption line will at periods of spot maxima appear brighter. In fact, the greater ray-curving, which marks these periods, enhances the shadowy background, but at the same time it restores the light to the central parts of the band. Thence the impression that the absorption line has been weakened.

On the other hand, lines with a faint, narrow background will at times of maxima appear considerably strengthened, because their brighter central parts, if present, are too narrow to be visible.

The explanations here given are supported by the results of an experimental investigation, a detailed account of which will appear elsewhere. Our object was to ascertain the action of a system of artificial surfaces of discontinuity on the absorption spectrum of sodium vapour. In principle the apparatus is similar to that described in my paper: "On maxima and minima of intensity sometimes observed within the shading of strongly widened spectral lines<sup>1)</sup>." A beam of electric light, which had first been passed through a long sodium flame was directed on the slit of a big grating spectroscope. But a great improvement had been since made in the burner. The aperture is 75 c.M. long and 0.15 c.M. wide: the supply of an adjustable mixture of gas and air is so regulated that the flame burns evenly over its whole length. A special contrivance within the burner allows of the feeding of the flame with sodium vapour during the experiment and regulating the quantity as required.

By means of this instrument we tested the effect on the absorption spectrum of the variations in the angle of inclination between the planes of discontinuity and the beam of light; of modifications in the quantity of sodium vapour; of diaphragms on the path of the rays, etc. All the phenomena observed may be explained

<sup>1)</sup> W. H. JULIUS, Proc. Roy. Acad. Amst. V, p. 665.

from the different measure in which the anomalously dispersed rays are curved; and the varying peculiarities of the sun-spot spectrum are easily reproduced in this experiment. We make particular mention of the fact that, when the flame is parallel to the beam of light, a small quantity of sodium vapour produced very dark enhanced D lines, e. g. 0.5 or 1 Angstr. units wide; by adding more of this vapour the lines extended into very wide bands in which the central portions became gradually brighter, leaving only a narrow, well-defined central absorption line.

### III. THE PERIODICAL VARIATIONS IN THE APPEARANCE OF THE SUN.

#### 1. *Sunspots and faculae.*

In a communication dated Febr. 1900<sup>1)</sup> I started the hypothesis that sun-spots are the results of refraction, more especially of anomalous dispersion. Since then EBERT<sup>2)</sup> has published an experiment in which, through the dispersion of the light of an arc lamp in a flame of burning sodium, effects were produced, closely resembling the phenomena observed in sun-spots, such as their spectral peculiarities, reversals, displacements, ramification of the lines, etc.

I have recently repeated this experiment, but instead of using pieces of burning sodium, I employed the long flame, which afforded greater facility for controlling the operation and noting the phenomena. They were substantially the same as those observed by EBERT.

Moreover, the use of the long flame enabled us to make some observations with respect to the optical effects of almost flat surfaces of discontinuity. Similar surfaces being important factors in our theory, a short description of our experiment may be found useful.

The light of an arc lamp was concentrated on a diaphragm 15 m.M. in diameter, which was placed almost in the focus of a second lens. The emergent rays were slightly divergent; within this beam, at a distance of 20 M., a telescope was placed and focussed on the lens. By pushing out the eye-piece an enlarged image of the lens was projected on a screen; this represented the Sun. Between the lens and telescope, but close to the former, was placed the long flame. When the mouth of the burner was so adjusted as to lie exactly parallel to the axis of the beam, so that the prolongations of the surfaces of discontinuity intersected the objective of the telescope,

1) Proc. Roy. Acad. Amst. II, p. 585—587.

2) H. EBERT, Die anomale Dispersion glühender Metaldämpfe und ihr Einfluss auf Phänomene der Sonnenoberfläche. Astron. Nachr. 155, S. 179—182.

there appeared on the screen a system of two very dark spots, corresponding to the two sheets of the flame, in which the combustion principally takes place. Even a slight change in the position of the burner had a marked effect on the form of the spots. By turning it a few degrees round a vertical axis the distinct spots rapidly disappeared; but then, of course, over a larger space of the illuminated surface quivering shadows of varying intensity remained visible.

Let us now more fully consider, what, in the present state of our knowledge, we may take the structure of the gaseous Sun to be. We find there the surfaces of revolution, first described by EMDEN <sup>1)</sup>, surfaces of discontinuity, where according to v. HELMHOLTZ undulation and formation of whirls take place. It is not unreasonable to suppose that the striped appearance of the corona presents to us, in some way, the generatrices of these surfaces, although at present we cannot enter into the question of how this takes place.

As a rule it will be found that the density varies most rapidly in the direction perpendicular to the planes of discontinuity; and wherever the whirling process is going on, the density will be least in the axes of the whirls.

In broad terms, therefore, the structure of the Sun may be called *lamellar* and at the places where whirls are formed, we would rather call it *tubular*. The position of the whirls in the surfaces of discontinuity is varying, but the average direction of the axes of the whirls coincides with the generatrices of the surfaces of revolution.

The prolongations of some of the surfaces of discontinuity intersect the Earth; whenever this happens, our line of sight, when directed on the Sun, very nearly touches a sheet of such a surface. These sheets are projected on the Sun's disc in the form of bands of greater or lesser width, stretching parallel to its equator. The narrower these bands are, the nearer our line of sight really touches the surfaces of discontinuity and the greater will therefore be the effect of refraction, i. e. the dispersion especially of the anomalously refracted light. The width of these projections on the various parts of the Sun's disc will of course vary with the position occupied by *P* on the sphere *B*.

If the axis of a whirl falls exactly in the line of sight, we see a dark speck. In parts where the whirling process is very active, the separate axes of the vortices need not be parallel to each other, but it is essential that they should all lie in the surfaces of discontinuity. This explains why a spot, i. e. an accumulation of a great

<sup>1)</sup> R. EMDEN, Beiträge zur Sonnentheorie. Ann. d. Phys. [4], 7, p. 176—197.

many whirls, notwithstanding the Sun's rotation, may remain visible for a long time, although continually changing its form, for we really look along a succession of other axes of whirls. The experiment described above, may serve to illustrate the fact that whirls, situated in surfaces of discontinuity which are not projected in very narrow bands, will *not* be seen as distinct spots. This is e. g. the case with whirls, formed at more than  $30^\circ$  heliographic latitude. Near the equator also spots are rarely seen; but this follows, according to EMDEN'S theory, from the circumstance that in those regions there is less cause for the formation of whirls.

To resume, spots will be seen in those parts where the distribution of matter is such as to cause an abnormal *increase* in the divergency of the beams of light on their way to the Earth. As a matter of course, there must also be parts where the distribution of density causes a *decrease* in divergency and these are the places where *faculae* are seen. On a smaller scale we find the same contrast in the so-called "pores and granulations" of the photosphere. All these solar phenomena are subject to rapid changes, because the complicated optical system through which the rays of light reach us, continually alters its position with respect to the Earth.

*The periodicity of the sun-spots.* We will now endeavour to prove that in order to explain the 11-year period in the frequency, the total spotted area and the mean heliographic latitude of the sun-spots, we need not admit the hypothesis of a periodical change in the Sun's "activity".

Let us for a moment suppose that all actual changes in the form of the Sun suddenly came to a stand-still, but that its rotation continued; even *then* an  $x$ -year period would be observable in the Sun's appearance, the position of spots and faculae etc., because each time, after  $x$  years have elapsed, the point  $P$  follows again nearly the same path.

However, the real configuration of the Sun is *not* perfectly constant (although probably its change is very slow and gradual) and so we may consider the 11-year period to be the result of the joint action of a *continuous* (perhaps somewhat irregular but not necessarily periodical) *change in the Sun's surfaces of discontinuity*, together with *the periodical variation in the position of the Earth with respect to the "average rotating sun"*.

We define the meaning of this latter expression by our sphere  $B$ , whose synodical period of revolution coincides with the period of circa 26 days, which has been noted in *terrestrial* phenomena.

It seems expedient here to enter somewhat further into the question as to how the periodical change of position of our point of view may cause the number of spots seen in the course of a year gradually to decrease for a period of 6 or 7 years, then to go on increasing, till after 11 years the maximum is reached again.

With that object we again refer to our spiral and start from the 14 convolutions of the year of spot maximum.

The second year's spiral is slightly shifted with respect to that of the first, but it runs still very close to it and therefore its position with regard to the system of surfaces of discontinuity will resemble that of the first, which was the *most favourable* for the observation of spots; thence we may conclude that the difference between the number of spots seen in the first and second year will be but small.

The spiral of the third year diverges again from that of the second and is consequently somewhat farther removed from the spiral, which traversed the series of optical combinations most favourable to the observation of spots, and so on.

We must not lose sight of the fact that the track of  $P$  has but a slight inclination with respect to the surfaces of discontinuity, so that at one time the Earth may remain for a rather long while under the influence of such surfaces, at other times, during much longer periods still, may pass between them.

There is no reason to expect that the decrease in the number of spots seen will proceed in a perfectly regular manner, but at all events there must be a year-spiral in which the circumstances are most unfavourable for their observation; for in proportion as the twelfth spiral is approached, which nearly coincides with the first, the conditions must necessarily again improve.

The length of the spot period is irregular and the height of the maxima varying. This would already be the case, were the Sun totally stationary, for the twelfth spiral of  $P$  does not exactly coincide with the first; besides it is evident that modifications in the distribution of matter may cause even greater irregularities in the successive fluctuations.

## 2. *Prominences.*

On a former occasion <sup>1)</sup> we have already given an explanation of the appearance of prominences and their spectral peculiarities, based on our hypothesis that they are due to the anomalous dispersion of the photosphere light in the whirling parts of the surfaces of discon-

<sup>1)</sup> Proc. Roy. Acad. Amst. IV, p. 162.

finity, which are seen projected on the edge of the Sun's disc. It will now be easy to determine in how far they are connected with spots and faculae and to understand, that, like the spots and for the same reasons, they may be expected to show a certain periodicity in their frequency and place of appearance.

The so-called metallic or eruptive prominences are only seen in the vicinity, at least in the zones, of the sun-spots, never in the polar regions. Nebulous prominences, on the contrary, are found in all latitudes. In accordance with our theory this fact may be thus explained. The anomalous dispersion of the kinds of light found in the spectrum of the metallic prominences near the lines of *Na*, *Mg*, *Ba*, *Fe*, *Ti*, *Cr*, *Mn*, is less intense than that of the light close to the lines of *H*, *He*, *Ca*; and therefore greater differences in density will be necessary to produce eruptive than nebulous prominences (in which as a rule only the lines of *H*, *He* and *Ca* are seen). The results of EMDEN's investigation in fact prove, that a more active formation of vortices may be expected in medial latitudes than in the equatorial or polar regions.

The zones where prominences appear must extend farther than those where spots are seen; for as soon as we have gained a clear conception of the direction of the surfaces of discontinuity and of the axes of the whirls in them, it becomes plain that to see spots, the position of the Earth with respect to the structural elements of the Sun is subordinate to preciser conditions than in the case of prominences. For prominences are visible as soon as the line of sight, directed on the apparent edge of the Sun, passes closely along a series of whirls; more particularly so, when the line of sight touches the surface of discontinuity near the whirling area. In order to see spots it is not only essential for the line of sight to touch the surface of discontinuity in the area of the whirls, it must at the same time coincide with the direction of their axes.

*The periodicity of prominences.* The parts of the Sun's edge where at a given moment the prominences appear, will not only be determined by the condition of the Sun itself, but at the same time by the position of *P*. Consequently the periodicity in the frequency and position of the prominences must agree with the periodicity of the motion of *P*.

A graphic survey of the periodicity of spots and prominences in connexion with their heliographic latitude has been given by Sir N. LOCKYER and W. J. LOCKYER<sup>1)</sup> in a paper on "Solar prominences and spot circulation from 1872—1901." In some of their former communications<sup>2)</sup> the same observers had already alluded to the fact

<sup>1)</sup> Sir N. LOCKYER and W. J. S. LOCKYER, *Nature* 67, p. 569—571, (1903).

<sup>2)</sup> The same authors, *Nature* 66, p. 249; 67, p. 377.

“that the epochs of maximum prominence disturbance in the higher latitudes are widely different from those near the equator. The latter are closely associated with the epochs of maxima spotted area, the former occur both N. and S. at intervening times.”

Now it follows from our theory, that prominences are seen in places where the line of sight touches whirling parts of surfaces of discontinuity near the Sun's edge; so it is evident that at spot maxima this will happen most often in the spot zones, and that the most favourable occasions for seeing them in other latitudes fall at other times.

Therefore, although in the curve of prominence frequency the 11-year spot period is easily recognized, yet in several points it deviates from the spot curve. Smaller maxima and minima of frequency are superposed upon the head curve and point to a three-year period. We find a rational explanation for these minor fluctuations too in the successive positions assumed by the Sun with respect to the Earth.

#### IV. THE PERIODICITY IN THE VARIATIONS OF METEOROLOGICAL AND EARTH-MAGNETIC ELEMENTS.

##### 1. *Do these phenomena require the hypothesis that the Sun exhibits a varying activity?*

In the preceding pages we ascribed the inconstancy of the solar phenomena principally to the continuous change of the point of sight from which we look at the Sun. We supposed the modifications, produced in the general condition of the body of the Sun itself by radiation and by the relative motion of the gaseous layers, to be comparatively slight and regular. Our theory had no need of the interference of violent eruptions, commotions, periods of increased or decreased solar “activity”; it allowed us to consider the quantity of energy emitted by the Sun in a unit of time, to be almost constant.

For this reason it would now at first sight seem more difficult yet to account for the periodical variations of several terrestrial phenomena which closely follow in their course the frequency of spots and prominences. But even with the hypothesis of a variable solar output as a starting point, as far as I know, not a single theory has been advanced in explanation of the connexion between sun-spots and terrestrial phenomena, so convincing, that it would be a pity to abandon it.

Let us briefly consider what has been attempted in that direction.

Periods of maximum spot frequency are marked by certain commotions on Earth and by increased circulation; the rainfall is greater,

cyclones, polar lights, magnetic deflections are more frequent. But because at those times the mean temperature over the entire Earth is somewhat lower than in the minima periods<sup>1)</sup> we come to the conclusion that the total energy which reaches the Earth in maxima of spot cycles must actually be less. This is our first objection to any explanation based on a periodical variation in the total output of the Sun's energy.

Now it might happen that, although in years of spot maxima the average output of solar energy be lessened, the emission exhibits at those times a greater variability than at minima. Various and numerous observations have been undertaken with the object of ascertaining whether the appearance of spots and faculae, or their crossing the central meridian of the Sun, was generally accompanied by excessive manifestations of terrestrial phenomena, and the results proved that this was *not* invariably the case. An exhaustive inquiry into this question has been recently made by A. L. CORTIE<sup>2)</sup>. The investigations of FATHER SIDGREAVES, extending over the years 1881—1896, had already clearly shown that periods of increased solar activity were indeed marked by violent magnetic storms, but that many spots were not accompanied by magnetic disturbances and that such disturbances often took place when the Sun was spot-free. "These results", says CORTIE, "are adverse to any theory which would place the cause of magnetic storms, and by the cause we mean the efficient cause, anywhere on or in the vicinity of the Sun." He himself for three years (1899—1901) studied the appearances of the Sun's face in connexion with the magnetic curves registered at Stonyhurst. He found that the *annual means* of spotted area and of the variations in declination fairly agreed; but his table on p. 207 shows that this is not the case when the average results for each single solar rotation are studied; and the immediate comparison of the daily solar observations with the diurnal magnetic curves shows more clearly still, that spots and disturbances do not necessarily always go together. For example, during a great magnetic storm on Febr. 12<sup>th</sup> 1899, the Sun was almost entirely free from spots, and the very large spot observed in May 1901, which persisted during two solar rotations, was not accompanied by any unusual magnetic disturbance. CORTIE comes to the conclusion that sun-spots and magnetic storms probably are correlated as "two connected, though sometimes independent effects of one common cause."

<sup>1)</sup> Cf. NORDMANN, C. R. 136, p. 1047—1050, 1903.

<sup>2)</sup> A. L. CORTIE, S. J., *Astrophysical Journal* 16, p. 203—210, 1902.

If, therefore, spots and faculae are not in themselves the factors which by their peculiar radiation of light and heat cause the supposed fluctuations in the output of solar energy, it might be expected that entirely different agencies play the most conspicuous part in the production of the phenomena under consideration.

In this sense ARRHENIUS<sup>1)</sup> has started an hypothesis in which the latest discoveries in connexion with the cathodic rays, the ionisation of gases, the properties of ions and electrons and the pressure of radiation have been introduced. He attributes the said periodical phenomena on Earth to solar matter, charged with negative electricity and being propelled from the Sun's surface by certain centres of activity there present (thus accounting for the period of 25,929 days). The amount of electricity thus generated varies with the Sun's activity, it being greatest at maxima of spot frequency. This solar matter is scattered through space by the pressure of radiation and causes the higher layers of the terrestrial atmosphere to be charged with negative electricity. By the discharges cathodic rays and polar lights are produced; the electrified particles, carried along by the wind, form electrical currents which disturb the magnetism of the Earth.

Several points of this theory have been criticised by CH. NORDMANN<sup>2)</sup>, who offers an entirely different explanation for the variable influence of the Sun on meteorological phenomena. He ascribes it to *long electrical waves*, sent out by the Sun, more particularly in the regions of spots and faculae, and at times of maximum spot frequency. Whenever these Hertzian waves penetrate into the higher layers of the atmosphere, they increase their conductivity and render them luminous. In this manner he accounts for the fact that during spot maxima stronger electrical currents are present in the atmosphere, magnetic variations are more marked and polar lights more frequent and intense.

But we have seen before that neither important magnetic disturbances nor intense polar lights invariably accompany very conspicuous solar phenomena. NORDMANN's theory therefore requires the admission of the existence on the solar surface of separate emission centres of long electric waves, independent of spots and faculae. This hypothesis does not simplify our conception of the constitution of the Sun.

BIGELOW<sup>3)</sup> ascribes the influence of the Sun on the magnetism of

1) ARRHENIUS, Rev. gén. d. Sc. 13, p. 65—76; Lehrb. d. kosm. Physik, S. 149—155.

2) CH. NORDMANN, Rev. gén. d. Sc. p. 379—388.

3) BIGELOW, Solar and Terrestrial Magnetism, U. S. Weath. Bur. Bulletin No. 21, 1898; Eclipse Meteorology and Allied Problems. Washington 1902. p. 104.

the Earth for the main part to direct magnetic action of the Sun; he supposes the magnetic condition of the Sun to be very variable. But as Lord KELVIN<sup>1)</sup> has demonstrated that the solar magnetism and its variability ought to be enormous to produce, by direct induction, these disturbances of the terrestrial magnetism, BIGELOW also admits a variable generation of electricity in the higher layers of the atmosphere, through the ionising action of the Sun's inconstant radiation. These views of BIGELOW have been analysed and criticised by SCHUSTER<sup>2)</sup>.

All these theories fail in one important point. Indeed, the meteorological and earth-magnetic disturbances generally manifest themselves in such a manner that they cannot be considered simply an increase or decrease of normal activity. For instance in the case of magnetic storms, the disturbance-vector is entirely out of keeping with the normal daily variations. The capricious origination and course of the barometric depressions, which play so prominent a part in determining the weather conditions in many parts of the globe, cannot be explained as merely resulting from increased ordinary atmospheric circulation; and many more examples might be added to these.

We must therefore consider the nature of the cosmic influence to be such, that, although emanating from the Sun and striking the Earth within cones whose opening is only 17,6" wide, it notwithstanding acts very differently in the various regions of the globe. Moreover, this influence distinctly shows a semi-annual periodicity. As yet no theory, based on the conception of a variable solar output, has been found to account for these striking characteristics of the cosmic influence.

If then, in order to explain the periodicity of *solar* phenomena, it has not been necessary to admit a varying activity of the Sun, we need not be deterred from accepting this conclusion by the consideration that it implies the abandoning of all prevailing ideas as to the influence of the Sun's activity on meteorological disturbances.

## 2. *Effects of the movement of the Earth through the irregular field of the Sun's radiation.*

When the rays of the Sun fall through a piece of ordinary window-glass on a distant screen, we notice an irregular distribution of light. In the same manner we imagine the rays proceeding from the inner parts of the Sun, after traversing the outer and thinner layers,

<sup>1)</sup> LORD KELVIN, *Nature* 47, p. 107--110. (1892).

<sup>2)</sup> SCHUSTER, *Terrestrial Magnetism* 3, p. 179--183, (1898).

to spread with unequal intensity through space. Consequently the Earth moves through an irregular field of radiation. And although we know the refractive power of the coronal gases to be but small, still we may assume that those kinds of rays, which undergo anomalous dispersion, will be liable to a rather strong incurvation and their beams to variation in divergency, especially in those places where they travel closely along the surfaces of discontinuity.

On this principle we base our explanation of the periodically varying influence, which an almost unchanging Sun exercises on terrestrial phenomena.

*A. The semi-annual and annual periods in the position of the Earth in the irregular field of radiation.*

At great distances from the centre of the Sun the surfaces of discontinuity become nearly flat. Those which are near the plane of the equator will be almost parallel to it. This assumption is in harmony with the appearance of the structural lines of the outer corona as well as with theoretical considerations.

If now we suppose the surfaces of discontinuity to be (geometrically) prolonged to the orbit of the Earth, it is evident that they will intersect its surface in a series of parallel circles, but the position of these circles with regard to the parallels of the Earth, will change with the position of the Earth in its orbit. Let us consider some particular positions.

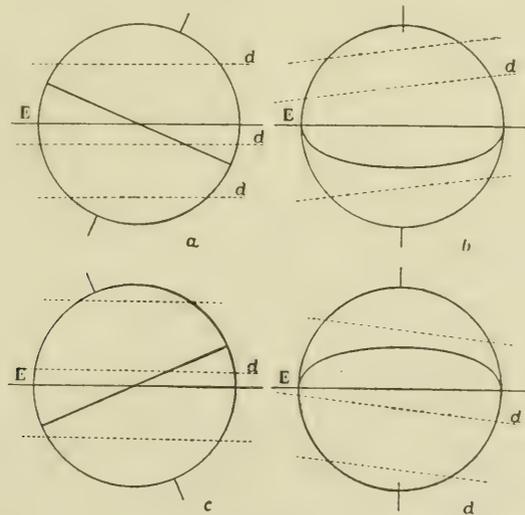


Fig. 2.

Fig. 2, *a* represents the position of the Earth on the 21<sup>st</sup> of March, as seen from the Sun. In the spring the Sun's south pole is

turned towards the Earth: on the 5<sup>th</sup> of March the Earth moves through that point of its orbit which lies farthest from the plane of the Sun's equator. In our diagram the latter might therefore be represented by a line running almost parallel to the ecliptic  $E$ , at a little over  $7^\circ$  heliographic latitude to the north of it. (The radius of the Earth is only  $8''$ ,8). The prolongations of the planes of discontinuity at  $7^\circ$  south of the Sun's equator being still almost parallel to it, their position may be indicated by the dotted lines  $d$  which, on the 21<sup>st</sup> of March, are only slightly inclined to  $E$ .

In Fig. 2,  $b$  we see the illuminated hemisphere of the Earth on the 21<sup>st</sup> of June. A short time before, on the 4<sup>th</sup> of June, the Earth passed through the nodal line of the Sun's equator and the ecliptic, so that, on the 21<sup>st</sup> of June, the planes of discontinuity  $d$  may still be represented by lines with an inclination of about  $7^\circ$  to the ecliptic.

Fig. 2,  $c$  shows the position on the 22<sup>d</sup> of September; at that date the Sun's equator lies south of the Earth.

Fig. 2,  $d$  represents the position of the Earth on the 21<sup>st</sup> of December.

From these diagrams it is plain that about the time of the equinoxes any point on the strongly illuminated parts of the Earth (we except those places where the Sun stands low) in its diurnal rotation always moves in the same sense with regard to the planes of discontinuity, making with them rather large angles (about  $23^\circ$ ). But soon after the solstices, in the beginning of July and January, at midday the said point will move about parallel to the planes of discontinuity; in the morning and in the afternoon its movement with regard to these planes is in contrary directions.

Now, as in the system of the surfaces of discontinuity the most rapid changes of density occur in a direction perpendicular to the surfaces, it follows that any point on the Earth, in its diurnal movement, will pass through a greater variety of conditions in spring and autumn than in winter and summer.

Besides it is evident that the variations in the said conditions will be less marked in the winter than in the summer solstice, because in the former season the days are so much shorter.

We may therefore expect an annual variation in the amplitude of certain daily inequalities showing the following periodicity:

maximum	end of March
minimum	beginning of July
maximum	end of September
minimum	beginning of January

whilst, especially in the temperate zones, the winter minimum will be lower than that of the summer.

Let us here once more call to mind the optical significance of the surfaces of discontinuity. As a rule they impart a greater divergence to the beams of light which travel closely along them; consequently at their intersection with the surface of the Earth they determine zones where the illumination will be weakened, whilst in the intermediate regions it will be strengthened. This does not apply in the same measure to every kind of light in the spectrum, but especially to the waves which undergo anomalous dispersion.

All terrestrial phenomena which are governed by the conditions of illumination will therefore, to a greater or lesser extent, be subordinate to the above-mentioned periodical variations.

There is probably still another reason for the greater variability of the effects of radiation in spring and autumn than in summer and winter. It is namely not improbable that in regions  $6^{\circ}$  or  $7^{\circ}$  distant from the Sun's equator greater differences of density will be found along the surfaces of discontinuity, than in the equatorial zones.

*B. The periodicity of the fluctuations of illumination which coincides with the periodicity of solar phenomena.*

In the course of a certain number of years the Earth describes through the system of the surfaces of discontinuity a somewhat complicated path, which we have represented by the track of  $P$  on the sphere  $B$ . The Earth therefore continually comes under the influence of another portion of the system; and the phenomena appearing on the Sun inform us whether, in a certain space of time, the light on its way to the Earth passes more or less often closely along surfaces of discontinuity. For this circumstance is intimately connected with the frequency of prominences and sun-spots and with the aspect of many of the FRAUNHOFER lines (especially in the spot spectrum). A so-called "maximum of solar activity" means, that the Earth during that period has been many times intersected by the prolongations of sharply defined surfaces of discontinuity, and all the terrestrial phenomena resulting from the variations of illumination will then also be at a maximum.

As to the nature of the connection between sun-spots and prominences on the one hand and the values of meteorological and magnetic variations on the other, it has been universally conceded that no other definition was possible but this: "that they were the effects of one and the same common cause."

We believe to have found this common cause in the varying

position of the Earth with respect to the surfaces of discontinuity and in the fluctuations in the conditions of illumination resulting from it.

Not only the fluctuations in the total intensity of illumination, but the changes in the composition of the solar light also, will have their significance in this respect.

### 3. *Polar lights.*

Polar lights belong to that class of phenomena which seem but little influenced by the local conditions on the surface of the Earth. The altitude at which they originate has been variously estimated; it is generally supposed to be very high, several kilometers. No one doubts but that this phenomenon is closely connected with the solar radiation, an opinion supported by the existence of a daily period with its maximum at 2<sup>h</sup>40<sup>m</sup> p. m. and its minimum at 7<sup>h</sup>40<sup>m</sup> a. m. (CARLHEIM-GYLLENSKIÖLD). Most probably polar lights owe their origin to the discharges of electricity generated during the day in the higher layers of the atmosphere through the ionising action of the Sun's irradiation.

If this be so, local differences in the Sun's irradiation must favour the appearance of polar lights and consequently we may expect in their frequency the semi-annual and annual periods described under *A* as well as the less regular variations spoken of under *B*.

The following table, taken from the *Lehrbuch der kosmischen Physik* by ARRHENIUS, p. 913, gives a survey of the frequency of polar lights from the enumerations made by EKHM and ARRHENIUS for various parts of the globe.

	Sweden. 1883—1896.	Norway. 1861—1895.	Iceland and Greenland. 1872—1892.	U. States of N. America. 1871—1893.	Southern Polar lights. 1856—1894.
January	1056	251	804	1005	56
February	1473	331	734	1455	126
March	<b>1312</b>	<b>335</b>	613	1396	<b>183</b>
April	568	90	128	<b>1724</b>	148
May	170	6	1	1270	54
June	10	0	0	1061	40
July	54	0	0	1223	35
August	191	18	40	1210	75
September	1055	209	455	<b>1735</b>	120
October	<b>1114</b>	<b>353</b>	716	1630	<b>192</b>
November	1077	326	811	1240	112
December	940	260	<b>863</b>	912	81

The last two columns distinctly show the expected periodicity: maxima in March or April and in September or October, minima in June or July and December or January, whilst in each case the winter minimum is lowest, although the long winter nights favour the observation of polar lights. In the other three columns, dealing with higher latitudes, the summer maximum, as ARRHENIUS observes, is only apparently so low, because in these regions no time is left for the observation of polar lights owing to the length of the days.

The data collected by FRITZ and ARRHENIUS (*Lehrb. d. kosm. Phys.* p. 915), moreover afford sufficient evidence that the sun-spot period too is reflected in the frequency of polar lights.

#### 4. *The annual variation in the diurnal inequality of terrestrial magnetism.*

It is an acknowledged fact that the magnetism of the Earth is under the influence of the Sun's irradiation. In recent years this view has been strengthened by the appearance of magnetic disturbances within the belt of totality during total eclipses of the Sun.

Let us suppose the mean magnetic force at every point of the Earth to be represented by a vector. If we now represent the daily variation by an additional, variable vector, the whole of all these additional vectors will form the "variation field". SCHUSTER and v. BEZOLD have computed and constructed this field and shown that by its movement from east to west with a velocity of  $15^\circ$  an hour, a fairly accurate idea may be obtained of the diurnal deflections of the magnetic needle on all parts of the Earth.

This "variation field", according to SCHUSTER, is formed for about  $\frac{3}{4}$  parts by electrical currents in the atmosphere and for  $\frac{1}{4}$  part by Earth currents. By the electrical current in the atmosphere we understand a convection current formed by electrified particles, which are carried along by the cyclonic and anticyclonic movements of the general circulation.

This theory of SCHUSTER and v. BEZOLD therefore implies that the diurnal magnetic variations will increase both with the intensity of the general circulation and with the amount of ionisation in the higher layers of the atmosphere. If one or both of these processes are in a great measure influenced by the variability of solar irradiation (which is not improbable, vide ARRHENIUS, *Lehrbuch* p. 886, 888, 890, 898), then all the periods which according to our theory occur in the variability of the Sun's irradiation must find their counterpart in the diurnal inequality of the elements of terrestrial magnetism.

A clear and concise exposition of the variations of terrestrial magnetism has been recently published by CHREE<sup>1)</sup>. The "mean monthly range" of a magnetic quantity is according to his definition: "the difference between the greatest and least of the twenty-four hourly values in the mean diurnal inequality for the month in question, based on the five quiet days selected for the month by the Astronomer Royal". If this range be represented by  $R$  and if  $S$  means the number by which WOLFER expresses the sun-spot frequency, we have, according to CHREE, the following relation :

$$R = a + bS.$$

His investigation extends over the 11-year period 1890—1900. He divides the twelve months into three seasons: November to February: winter; March, April, September and October: spring and autumn; May to August: summer, and finds the following values for  $a$  and  $b$ .

	Declination.		Inclination.		Horiz. int.		Vert. int.	
	$a$	$b$	$a$	$b$	$a$	$b$	$a$	$b$
Winter	3.23	0.0323	0.63	0.0105	10.5	0.461	7.0	0.032
Spring and autumn	7.32	0.0478	1.26	0.047	23.5	0.221	17.2	0.026
Summer	8.91	0.0428	1.61	0.0137	30.6	0.190	22.7	0.035
Mean	6.49	0.0410	1.17	0.0130	21.5	0.191	15.6	0.031

$a$  marks the variability according to the seasons, irrespective of the spot-period.

$b$  shows in how far the influence of the spot-period depends on the seasons.  $S$  in the period under consideration oscillated between 0,3 and 129,2, its mean value being 41,7.

From the point of view of our theory these figures prove that :

$a$  in each element shows a minimum in winter and a maximum in summer; this we explain by the greater intensity of the Sun's irradiation in summer increasing both the general circulation and the generation of electricity. But the table shows also that the values of  $a$  in spring and autumn are invariably greater than the mean value for the whole year; this points to superposed *maxima during the equinoxes*, and this we ascribe to the way in which the variability of illumination is dependent on the position of the Earth's axis with respect to the surfaces of discontinuity, (periodicity  $A$  p. 289).

<sup>1)</sup> CHREE, Preliminary Note on the Relationships between Sun-spots and Terrestrial Magnetism, Proc. Roy. Soc. 71, p. 221—224, 1903.

In the values of  $b$  the periodicity  $A$  plays a far greater part than in those of  $a$ . That stands to reason: for the term  $bS$  less concerns the amount of the general atmospheric circulation, than it does the peculiarities of the surfaces of discontinuity in respect to the Earth.

In the values of the vertical intensity,  $b$ , as compared to  $a$ , has a far lesser significance than in those of the other three elements. CHREE makes the mean value of  $b$  over a whole year 100 and then arrives at the following values of  $b$  for the seasons.

	Declination	Inclination	Horiz. int.
Winter	79	81	85
Spring and autumn	117	113	116
Summer	104	106	99

Thus it appears that the amplitude of the diurnal inequality, taken absolutely, depends in a far greater measure on sun-spot frequency at the times of the equinoxes than at other times. The reason of this we find in the fact that the greater variety of sharply defined planes of discontinuity which at spot maxima intersect the Earth, causes greater diversity in its illumination when the projection of the diurnal motion on the normals to the planes is large, than when it is small. (Compare Fig. 2 p. 289).

Now, if we consider the influence of the spot frequency not absolutely, but in comparison with the influence of the annual variation taken for *average* spot frequency, a relative value which CHREE expresses by the quotient  $\frac{4,17b}{a}$ , then we obtain :

	Declination	Inclination	Horiz. int.
Winter	0.42	0.69	0.60
Spring and autumn	0.27	0.49	0.39
Summer	0.20	0.35	0.26

which shows that the influence of the spot frequency on the amplitude of the daily inequality is *comparatively* strongest in winter. This must be attributed to the fact that during a winter day the changes of position of a point on the globe with respect to the Sun and to the surfaces of discontinuity are proportionally small, and consequently the variations in illumination are then principally caused by irregularities, occurring in the system of the planes of discontinuity itself.

The investigations of CHREE were confined to the observations at KEW. A synopsis of the annual variations in the daily inequality of

the horizontal intensity, collected from the various readings in different parts of the globe between 1841 and 1899, will be found in Prof. FRANK BIGELOW'S "Studies on the Statics and Kinematics of the atmosphere in the U. S. of America", p. 56—57.

The figures tally in every respect with the above results.

### 5. *Magnetic disturbances.*

If now we apply the preceding arguments to the irregular disturbances or magnetic storms, their explanation will offer no difficulties.

We attribute these phenomena to extraordinary differences in density, which may at times be found on each side of the planes of discontinuity in the line connecting the Earth with the Sun. The system of the surfaces of discontinuity moves so rapidly with respect to the Earth, that almost all parts of the illuminated hemisphere are influenced simultaneously by the extraordinary local condition of the radiation field; whereas it is evident that the abnormal illumination at the same time may be more intense in some regions of the Earth than in others<sup>1</sup>). Consequently magnetic storms will be noticed everywhere almost simultaneously, and their effects will be almost identical in places lying rather close together, whilst, in regions farther distant from each other, they may be entirely different, perhaps quite opposite.

ELLIS has made a study of the annual variation in the frequency of magnetic disturbances and classed them into certain groups. "Strong disturbances", (over  $1^\circ$  in declination and 300 units of the fifth decimal in horizontal force) have two maxima, one in April and one in September; "weak disturbances" (10' and 50 units) show a maximum in summer and a minimum in winter. The characteristics of periodicity *A* (p. 289) at once strike us here, and it seems to us also to afford a satisfactory explanation in this case. Besides we find especially in the curve of the disturbance frequency an argument in favour of the opinion expressed on p. 291 viz. that along planes of discontinuity at  $6^\circ$  or  $7^\circ$  from the Sun's equator, greater irregularities in the distribution of density will be met with than in the equatorial zones. And in the diurnal period of the disturbances, which in the tropics shows a maximum at midday, we see another argument in support of this assumption.

After the explanations given under *B*, it will cause no surprise to recognize in the magnetic disturbances the periodicity of solar phenomena. There is but an indirect connexion between magnetic

<sup>1</sup>) The rapid changes noticed in HALE'S abnormal spectra support this view.

storms and sun-spots, faculae, prominences. Both kinds of phenomena depend on the presence of sharply defined surfaces of discontinuity, but the appearance of the solar phenomena is more particularly determined by the direction and divergency of the rays of light in the vicinity of the *Sun*, whereas the terrestrial disturbances rather depend upon the divergency of these rays nearer the *Earth*. Therefore it may often happen that magnetic storms coincide with the appearance of large sun-spots, or faculae, or prominences, but this is not an indispensable condition.

According to LOCKYER "great" magnetic storms are synchronous with maxima of prominence frequency near the poles of the Sun, whilst the curve for the mean variability of terrestrial magnetism is almost an exact reproduction of the curve for the prominence frequency in equatorial regions <sup>1</sup>).

This fact may be explained as follows. The appearance of prominences near the poles is the result of the optical effects of parts of surfaces of discontinuity which are strongly inclined on the plane of the equator. We may assume that similar parts will also produce irregularities in the radiation field, at the site where the Earth is situated, and that the structure of these irregularities will not be parallel to the principal structure, i. e. to the solar equator. In moving along the Earth they must give rise to stronger and more evanescent disturbances in the terrestrial magnetism than the irregularities corresponding to the normal lamellar structure, which makes but very small angles with the ecliptic.

#### 6. *The annual variation in the daily oscillations of atmospheric pressure.*

The polar lights and the variations of terrestrial magnetism are principally governed by conditions in the higher layers of the atmosphere and but little by those on the surface of the Earth. The barometric pressure, the temperature, the rainfall, the direction of the wind and all meteorological phenomena which accompany them, are to a considerable extent influenced by the distribution of land and water. Among local influences, cosmic action therefore, will not be prominent in these latter phenomena.

In the higher layers of the atmosphere the matter becomes much simpler. A short time ago BIGELOW <sup>2</sup>) has called attention to the fact that

<sup>1</sup>) LOCKYER, C. R. 135, p. 361—365, (1902); Proc. Roy. Soc. 71, (1903).

<sup>2</sup>) BIGELOW, Studies on the Meteorological Effects in the Un. States of the Solar and Terrestrial Physical Processes. Weather Bureau No. 290, Washington 1903.

the well-known semi-diurnal period in the pressure, the atmospheric electricity, the vapour tension and the absolute humidity, disappears in proportion as higher layers of the air are examined and resolves itself into a simple diurnal period, having its minimum about 3<sup>h</sup> a. m. and its maximum at 3<sup>h</sup> p. m.

However it is only in recent years that a systematic investigation of the higher layers of the atmosphere has been undertaken, principally in N. America and in Germany, and the results published until now are insufficient to deduce from them the cosmic periods. Anyhow, the same annual variation as that which marks the polar lights and the terrestrial magnetism has been observed in the diurnal oscillation of barometric pressure near the surface, notwithstanding the complexity of the influences there at work.

The table here subjoined, taken from the handbook of ARRHENIUS p. 603, gives the mean amplitude of the semi-diurnal oscillations of the barometer, expressed in m. m., for the following places:

1) Upsala 59°52' n. lat., 2) Leipzig 51°20' n. lat., 3) Munich 48°9' n. lat., 4) Klagenfurt 46°37' n. lat., 5) Milan 45 28' n. lat., 6) Rome 41°52' n. lat., 7) 22°30' s. lat., 8) 10° n. lat.

	Jan.	Febr.	March	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Year
1)	0.43	0.44	0.15	<b>0.16</b>	0.14	0.13	0.13	0.14	<b>0.17</b>	0.15	0.11	0.10	0.13
2)	0.46	0.20	0.24	<b>0.27</b>	0.22	0.20	0.21	0.23	<b>0.27</b>	0.22	0.21	0.16	0.22
3)	0.21	0.23	0.28	<b>0.29</b>	0.28	0.26	0.25	0.26	<b>0.28</b>	0.27	0.21	0.21	0.25
4)	0.23	0.29	<b>0.35</b>	0.26	0.26	0.25	<b>0.34</b>	0.27	0.27	0.24	0.21	0.24	0.27
5)	0.30	0.35	<b>0.38</b>	0.36	0.30	0.29	0.29	0.31	0.32	<b>0.33</b>	0.31	0.29	0.32
6)	0.30	0.33	<b>0.35</b>	0.32	0.29	0.26	0.26	0.30	0.35	<b>0.36</b>	0.33	0.29	0.31
7)	0.65	0.68	<b>0.70</b>	0.68	0.64	0.61	0.63	0.66	0.72	<b>0.72</b>	0.69	0.66	0.67
8)	0.79	0.80	<b>0.83</b>	0.82	0.73	0.65	0.65	0.69	0.75	0.78	<b>0.82</b>	0.79	0.76

It will be seen that the maxima again coincide with the equinoxes; that the winter minimum for places above 45° lat. is lower than the summer minimum, thus agreeing in every respect with the periodicity described under A. It is indeed easy to understand that the amplitude of the fluctuations in the atmospheric pressure will increase or decrease according as the variability of the illumination increases or decreases. The circumstance that in lesser latitudes, north as well as south of the equator, the July minimum seems lowest, is ascribed by ARRHENIUS to the fact that the Earth is at that time farther away from the Sun than in January.

7. *The annual and secular variations of atmospheric pressure.*

When we compare the system of isobars obtained for each separate month, it becomes at once apparent that the annual variation of the barometric pressure is very different in the various regions of the Earth. In the tropics the fluctuations are generally insignificant; in the central parts of the continents of the temperate zones the atmospheric pressure is low in summer and high in winter; in mid-ocean this is the reverse; beyond  $45^{\circ}$  lat. south the pressure is uniformly low; on the other parts of the globe the greatest diversity exists in its annual course.

Nevertheless most of the annual curves (especially those of the temperate zones) display, next to local peculiarities, a common characteristic. They exhibit, more or less distinctly, two minima at the times of the equinoxes and maxima in winter and summer. The regions near the North Pole seem to make an exception to this rule (perhaps also those at the South Pole); there the maxima occur in spring and autumn and the minima in winter and summer.

Some important statistics in connexion with the atmospheric pressure in N. America have been published in the Report of the Chief of the Weather Bureau 1900—1901. Vol. II. Chapter X treats of the annual and secular variations; there we find the monthly deviations from the mean barometric pressure over a certain number of years (1873—1899) arranged by Prof. BIGELOW into 10 groups, according to the geographical position of the observation stations, and the mean annual course of these deviations charted for each group.

The ten curves thus obtained show great differences, due to the more continental or more maritime character of the region to which they refer, but all reveal a cosmic influence in showing minima at the times of the equinoxes and maxima during the solstices.

From our point of view this cosmic influence may be thus defined.

The greater variability in the Sun's irradiation during the spring and autumn increases the atmospheric circulation, and this augments the average horizontal velocity component of the air as well as the evaporation, and both processes cause the atmospheric pressure to decrease. In the polar regions the solar radiation exercises a lesser influence; in those parts compensation can take place and consequently the maxima occur in spring and autumn.

BIGELOW has also tabulated the same data in another manner. He has calculated for each station the successive yearly means and subtracted from them the check mean of the whole period (1873—

1899) thus obtaining 27 residuals. The stations were then again gathered into the same groups, this time only eight in number (because the observations for the West Indies were considered too incomplete) and for each group the 27 mean values of the residuals were computed.

The curves representing these mean residuals show for each of the eight districts the secular variations of atmospheric pressure in that region.

The eight curves certainly exhibit many differences when compared to each other: nevertheless in the number of their maxima and minima we observe such an unmistakable similarity, that it is evident they are acted upon by a common influence, the cosmic nature of which is not doubtful.

Similar charts have been framed by LOCKYER and by BIGELOW for other parts of the globe and compared with the curve of prominence frequency. They resulted in the conclusion that an undeniable relation exists between these phenomena.

However, to find this relation is not such a simple matter. In some regions of the Earth the maxima of prominence frequency coincide with the maxima of atmospheric pressure (Bombay, Batavia, Perth, Adelaide, Sidney), in others on the contrary with the minima (Cordoba, Mobile, Jacksonville, Pensacola, San Diego), whilst elsewhere again the maxima are shifted, although the general character of the curves persists.

As yet the barometrical observations undertaken in elucidation of this question are confined to too small a number of places to allow of general conclusions being drawn from the data collected. It is therefore under reservation that we emit the following hypothesis as a guide for further investigation.

At periods of maximum prominence frequency the atmospheric circulation is intensified owing to the irregularities of the solar radiation field. This causes a decrease of the mean barometric pressure at all those places, where the enhanced circulation causes an excess of humidity, whilst at places where this is *not* the case, the mean atmospheric pressure will be above the normal.

#### 8. *Cosmic influence on other terrestrial phenomena.*

If the Earth moved through a perfectly regular radiation field, there would be a certain normal atmospheric circulation, and in connexion with this circulation there would be at each place a fixed

and regular state of the weather, varying of course with its geographical position and the actual seasons, but otherwise recurring from year to year with only small accidental variations.

As things are, meteorological conditions are the reverse from reliable. We attribute their variability to the irregularity of the radiation field.

The peculiarities of the surfaces of discontinuity add their quota in determining the localities, where minima of atmospheric pressure will occur; they influence the depth and movement of the depressions, the course of the cyclones, the direction of the wind, the formation of clouds and the rainfall.

MELDRUM found that between the equator and 25° southern latitude, cyclones are more violent and more frequent at spot maxima than at minima. POEY established the same fact for the cyclones in the Antilles; and to this again it is attributed that in years of spot maxima during the spring, south winds are predominant in Western Europe; that less frosty days occur at that season, the ice melts at an earlier date than usual, the water-mark stands higher for the great rivers, plants are more forward, etc. (ARRHENIUS *Lehrbuch d. kosm. Phys.* p. 141—146).

Neither does it seem out of place to attribute the periodical alternations of years with much rain and years of drought in British India <sup>1)</sup>, which react in so conspicuous a manner on the economical condition of that country, to the periodicity in the varying position of the Earth with respect to the surfaces of discontinuity. An excess of rainfall seems there a regular occurrence within a three year period around the maximum and a three year period around the minimum of sun-spots. The intervening years are marked by drought, the cause of famine. The regular course of these meteorological phenomena was interrupted in 1899, when great drought and excessive famine coincided with a spot minimum; but at the same time the widened lines of the spot spectrum presented an abnormal appearance. Here again we find a circumstance in support of our assumption, that the irregularities of the mean atmospheric circulation are caused by the surfaces of discontinuity. However, similar local meteorological phenomena depend on so many conditions, that we dare not look forward to a speedy solution of the problems they present.

#### SUMMARY OF RESULTS.

Overlooking the results of this investigation we see that the prin-

<sup>1)</sup> Sir N. LOCKYER and W. J. S. LOCKYER, "On Solar Changes of Temperature and Variations in Rainfall in the Region surrounding the Indian Ocean". *Proc. Roy. Soc. London* 67, p. 409—431 (1901).

ciple of anomalous dispersion opens a way to account for the connection between solar phenomena and terrestrial disturbances.

There is a striking feature in the manifestations of solar influence on meteorological and earth-magnetic elements, which it is especially difficult to explain by other principles, namely the circumstance that this cosmical influence does not affect the illuminated hemisphere uniformly, but often appears to act variously on different regions of the Earth, although the solar parallax is only 8.8"

This peculiarity of the solar influence, as well as the divers periodicities observed in the variations of meteorological and magnetic elements, may be readily explained as consequences of the irregularities of the solar radiation field, which in their turn are caused by surfaces of discontinuity.

Our aim has been also to show, that even when supposing the solar output to be constant, periodical alterations in the frequency of spots, faculae and prominences and in the appearance of widened spectral lines must result from the mere change of the Earth's position relative to our rotating luminary. The 11-year period, especially, seems to follow as a natural consequence from these considerations.

It may be that we have touched here the only efficient cause of the periodicities noticed and that there really remains no ground for the admission of a variable solar activity. This latter inference we have, however, not proved, but for the sake of argument taken for granted.

**Zoology.** — "*The process of involution of the mucous membrane of the uterus of Tarsius spectrum after parturition.*" By Prof. HANS STRAHL of Giessen. (Communicated by Prof. J. D. VAN DER WAALS, on behalf of Prof. A. A. W. HUBRECHT).

I am indebted to Professor HUBRECHT for some exceedingly interesting specimens of uteri of *Tarsius spectrum*, which enable me to throw some further light on the different phases of the process of involution gone through by the uterus during this animal's puerperal period.

This material was especially valuable as I had an opportunity, on previous occasions, of examining the same process in a series of other mammalia, and I am now enabled to determine how far *Tarsius* agrees with the forms hitherto under observation, and where it differs from them.

I had a considerable number of uteri at my disposal, some from the

latest period of pregnancy; a great many dating shortly after delivery, others again of later date, and some showing the condition of the uteri in a non-puerperal or non-pregnant state.

Before summing up briefly, in this paper, the results of my experiments, I must at once point out that the involution process in the case of *Tarsius*, throughout its development, takes its own peculiar course and is unlike any of the other forms of mammals that have had the uterus carefully examined up to now.

As far as we know up to the present, we can divide the mammalia with so-called full-placenta, (all classified under the heading of deciduata in the old-fashioned terminology), into three groups according to the process of involution. In the species of the first group, to which man and the monkeys belong, the placenta is spread out flatly on the inside of the uterus while in the mucous membrane, which has turned into decidua vera, the epithelium is entirely absent.

In the second group the placenta is also spread out over the entire inside of the uterus, but in addition to this the womb is covered throughout with uterus epithelium. Such uteri are found in carnivores. In the rodents we often meet with the third form; here, towards the end of gestation, not only is the womb covered with cell-tissue, but this epithelium also runs from the fimbriae right underneath the placenta, undermining it till it is finally only adhering to the walls of the uterus by a slender cord, carrying the vessels.

It is evident that, — taken as a whole class, — the uteri of the 3<sup>d</sup> group will resume relatively quickly their non-puerperal appearance, while those of the first-named have to go through a complicated process of involution.

We may add at once that *Tarsius* belongs to the third group. The lumen of the uterus gravidus just before parturition was found to be entirely covered with epithelium which ran underneath the rim of the placenta towards the centre of it, up to the connecting tissue-string, carrying the vessels of the placenta.

As already described by HUBRECHT in his excellent work on the placenta of *Tarsius*, we find in this placenta-cord conglomerations of uterus-glands, the cell-tissue of which present every possible phase of involution, while others are covered with well-preserved cells. These remains of glands in the placenta play a prominent part in the puerperal involution.

In two of the puerperal uteri I find the placenta still existent; I think it possible that here it is so far a question of physiological and not of pathological circumstances, as perhaps the placenta,

instead of being at once thrust out after the parturition, has remained for a little while in the mother's genital ducts.

Once the placenta gone, the seat of the placenta in the mucous membrane of the uterus can be traced microscopically or by means of a magnifying glass for some considerable time. It is found to protrude above the surrounding mucous membrane like a round or oval-shaped body which I will call the placenta-bed.

This bed, as we learn from the microscopic preparations, is limited by the accumulation of the remains of the glands lying along the vessels situated in the placenta-cord, which I will give the name of "paravascular epithelial tubes" and in the centre of which the remains of the vessels of the placenta in a state of thrombosis, form a "placenta-plug".

By the side of the placenta-bed the mucous membrane forms little folds which often protude into the lumen of the uterus in the shape of vesicle-shaped cavities.

Among the changes that now set in during the process of involution we have to distinguish between those which take place independently, in the material at our disposal, and those which are noticeable from a topographical point of view.

As regards the first, even during pregnancy so much material has been accumulated for the formation of the new mucous membrane — the changes in which will only be described here — that it has now really become a question of elimination of the superfluous. It is especially epithileum which is got rid of, as far as dispensable, by its being shed.

Topographically two things are happening. At what used to be the seat of the placenta we find as paravascular epithelial tubes remains of uterus-glands, in considerable number, while in the other sections of the womb there is a small number only of these uterus-glands.

In both the uterus-horns of the non-puerperal uterus the glands which in this condition of the womb are of a narrow and elongated shape, run close together and are equally distributed, but this condition can only be arrived at by means of two simultaneous events: At the recent seat of the placenta the material of the large and wide paravascular vessels is almost entirely got rid of by its dying off. A little of it survives, to form the nucleus of fresh uterus glands.

In the other parts of the womb a large number of new glands are developing at the surface of the epithelium in the same way as the glands are growing during the time of pregnancy, namely

through the forming of small epithelium plugs, growing downwards from the surface.

And while the whole uterus is trying to regain its normal shape by means of contraction of all its muscles throughout, the mucous membrane must of course shrink considerably; this process follows new lines, different from those which I have so far met with in any of the puerperal uteri of mammalia, hitherto examined.

How this involution process progresses will be described in details by Dr. W. KERZ in an exhaustive work, freely enriched with illustrations, and in which due attention is paid to the works of reference written on the subject.

**Mathematics.** — “Series derived from the series  $\sum \frac{\mu(m)}{m}$ .” By Prof.

J. C. KLUYVER.

By  $\mu(m)$  we denote an arithmetical function of the integer  $m$ , which equals 0 if  $m$  be divisible by a square, and otherwise equals +1 or -1, according as  $m$  is a product of an even or of an odd number of prime numbers.

The series

$$\sum_{m=1}^{m=\infty} \frac{\mu(m)}{m} = 1 - \frac{1}{2} - \frac{1}{3} - \frac{1}{5} + \frac{1}{6} \cdot \cdot \cdot \cdot + \frac{1}{26} - \frac{1}{29} - \frac{1}{30} \cdot \cdot \cdot \cdot$$

was considered by EULER, who concluded that it converged towards 0, a theorem only recently proved by von MANGOLDT (1897) and by LANDAU (1899).

In this paper it will be shewn that in innumerable ways we may select from EULER'S series infinite groups of terms, each of these groups again constituting a convergent series.

In fact we may assume a linear congruence

$$x \equiv h \cdot \cdot \cdot \cdot \pmod{b}$$

and from EULER'S series retain only those terms the denominators of which are solutions of the congruence.

From

$$T_{1,0} = \sum_{m=1}^{m=\infty} \frac{\mu(m)}{m}$$

we get thus the new series

$$T_{b,h} = \sum_{m=0}^{m=\infty} \frac{\mu(mb+h)}{mb+h}$$

and it will be found that this series has a definite sum, whatever may be the integers  $b$  and  $h$  ( $h < b$ ).

Firstly consider the case  $h = 0$  and suppose  $b$  to be prime. As it is necessary to start with finite series we write,  $g$  being any positive number,

$$T_{b,0}^g = \sum_{m=1}^{mb < g} \frac{\mu(mb)}{mb} \quad , \quad T_{b,h}^g = \sum_{m=0}^{mb+h < g} \frac{\mu(mb+h)}{mb+h}.$$

Then, since  $\mu(mb)$  is either 0 or  $-\mu(m)$  according as  $m$  is divisible by  $b$  or not, we have

$$T_{b,0}^g = -\frac{1}{b} \sum_{h=1}^{h=b-1} T_{b,h}^g = -\frac{1}{b} \left( T_{1,0}^g - T_{b,0}^g \right),$$

or

$$T_{b,0}^g = -\frac{1}{b} T_{1,0}^g + \frac{1}{b} T_{b,0}^g, \quad . . . . . (A)$$

and in the same way

$$\begin{aligned} T_{b,0}^{\frac{g}{b}} &= -\frac{1}{b} T_{1,0}^{\frac{g}{b}} + \frac{1}{b} T_{b,0}^{\frac{g}{b}}, \\ T_{b,0}^{\frac{g}{b^2}} &= -\frac{1}{b} T_{1,0}^{\frac{g}{b^2}} + \frac{1}{b} T_{b,0}^{\frac{g}{b^2}}, \\ & . . . . . \end{aligned}$$

Supposing  $g$  to lie between  $b^z$  and  $b^{z+1}$  we infer from these equations

$$T_{b,0}^g = -\sum_{k=1}^{k=z} \frac{1}{b^k} T_{1,0}^{\frac{g}{b^k}} . . . . . (B)$$

Now it follows from the identity

$$1 = \sum_{m=1}^{m < g} \mu(m) \left[ \frac{g}{m} \right],$$

that

$$\sum_{m=1}^{m < g} \frac{\mu(m)}{m}$$

is always finite and less than 2; hence equation (B) gives

$$\left| T_{b,0}^g \right| < \frac{2}{b-1}$$

however large the number  $g$  may be, and taking this inequality into account it is seen from equation (A) that we have necessarily

$$T_{b,0}^g = \lim_{g \rightarrow \infty} T_{b,0}^g = 0.$$

The proof given here is easily extended to the case in which  $b$  is not prime but a product of unequal prime factors. Square factors are excluded, for then  $T_{b,0}$  is identically zero.

Let  $c$  be a prime number not dividing  $b$ , then instead of equation (A) we can establish the relation

$$T_{bc,0}^g = -\frac{1}{c} T_{b,0}^{\frac{g}{c}} + \frac{1}{c} T_{bc,0}^{\frac{g}{c}},$$

and it will appear that  $T_{bc,0}^g$  tends to zero, if we can show that  $\lim_{g \rightarrow \infty} T_{b,0}^g = 0$ . Now the latter theorem is proved for any prime number  $b$ , hence it must remain true if repeatedly we multiply  $b$  by other prime factors  $c$ .

In order to investigate the series  $T_{b,h}$  we consider the series of functions

$$\sum_{m=1}^{m=\infty} \frac{\mu(m)z^m}{1-z^m}.$$

Evidently it converges for  $|z| < 1$ , and expanding each term into a power series, we find

$$\sum_{m=1}^{m=\infty} \frac{\mu(m)z^m}{1-z^m} = \sum_{m=1}^{m=\infty} z^m \sum_{d|m} \mu(d) = z,$$

for the sum  $\sum_{d|m} \mu(d)$ , in which the summation is extended over all divisors  $d$  of  $m$ , unity and  $m$  itself included, is zero except for  $m = 1$ .

Similarly we have by changing  $m$  into  $mb$

$$\sum_{m=1}^{m=\infty} \frac{\mu(mb)z^{mb}}{1-z^{mb}} = \sum_{m=1}^{m=\infty} z^{mb} \sum_{d|m} \mu(bd).$$

Let  $b$  be the product of the prime factors  $p_1, p_2, \dots, p_k$ , then  $\sum_{d|m} \mu(bd)$  is zero but for those integers  $m$  that are of the peculiar form

$$p_1^{z_1} p_2^{z_2} \dots p_k^{z_k}, \text{ and in that case we have } \sum_{d|m} \mu(bd) = \mu(b).$$

Hence we may write

$$\sum_{m=1}^{m=\infty} \frac{\mu(mb) z^{mb}}{1-z^{mb}} = \mu(b) \sum_{z_1, z_2, \dots, z_k} z^{nb},$$

$$(n = p_1^{z_1} p_2^{z_2} \dots p_k^{z_k})$$

(a relation still holding for any  $b$  having square factors).

Integrating from the above equations we deduce

$$\sum_{m=1}^{m=\infty} \frac{\mu(m)}{m} \log(1-z^m) = -z,$$

$$\sum_{m=1}^{m=\infty} \frac{\mu(mb)}{mb} \log(1-z^{mb}) = -\mu(b) \sum_{z_1, z_2, \dots, z_k} \frac{z^{nb}}{nb}$$

and subtracting

$$\sum_{h=1}^{h=b-1} \sum_{m=0}^{m=\infty} \frac{\mu(mb+h)}{mb+h} \log(1-z^{mb+h}) = -z + \mu(b) \sum_{z_1, z_2, \dots, z_k} \frac{z^{nb}}{nb}.$$

Denoting by  $k$  a number less than  $b$  and prime to  $b$  I substitute

$$z = \rho e^{\frac{2\pi i k}{b}}$$

and afterwards make  $z$  tend to unity.

The righthand side ultimately takes the value of

$$\begin{aligned} -\rho e^{\frac{2\pi i k}{b}} + \frac{\mu(b)}{b} \sum_{z_1, z_2, \dots, z_k} \frac{1}{n} &= -\rho e^{\frac{2\pi i k}{b}} + \frac{\mu(b)}{b \left(1 - \frac{1}{p_1}\right) \left(1 - \frac{1}{p_2}\right) \dots \left(1 - \frac{1}{p_k}\right)} = \\ &= -\rho e^{\frac{2\pi i k}{b}} + \frac{\mu(b)}{\varphi(b)} \end{aligned}$$

where  $\varphi(b)$  indicates the number of integers less than  $b$  and prime to  $b$  and the equation itself may be written

$$\sum_{h=1}^{h=b-1} T_{b,h} \times \log \left(1 - \rho e^{\frac{2\pi i hk}{b}}\right) = -\rho e^{\frac{2\pi i k}{b}} + \frac{\mu(b)}{\varphi(b)} \dots \quad (C)$$

It implies  $k$  prime to  $b$ , but for other integers  $k$  less than  $b$  and not prime to  $b$  a similar equation can be established.

Suppose

$$\frac{k}{b} = \frac{k'}{b'}$$

where  $k'$  and  $b'$  are now prime to each other, then we have

$$\sum_{k'=1}^{k'=b'-1} T_{b',k'} \times \log \left( 1 - e^{\frac{2\pi i k' k'}{b'}} \right) = -e^{\frac{2\pi i k'}{b'}} + \frac{\mu(b')}{\varphi(b')}$$

But denoting by  $h$  all integers less than  $b$  that satisfy the congruence

$$h \equiv k' \dots (\text{mod. } b')$$

we have evidently

$$\sum_h T_{b,h} = T_{b',k'} \dots \dots \dots (D)$$

and also

$$\sum_h T_{b,h} \times \log \left( 1 - e^{\frac{2\pi i hk}{b}} \right) = T_{b',k'} \times \log \left( 1 - e^{\frac{2\pi i k' k'}{b'}} \right);$$

hence in case  $k$  is not prime to  $b$  we are led to the equation

$$\sum_{h=1}^{h=b-1} T_{b,h} \times \log \left( 1 - e^{\frac{2\pi i hk}{b}} \right) = -e^{\frac{2\pi i k}{b}} + \frac{\mu(b)}{\varphi(b)}, \dots (E)$$

if only we omit at the lefthand side the terms corresponding to those integers  $h$  that are multiples of  $b'$ . With this limitation the equation (E) applies to all values of  $k$ , for if  $k$  be prime to  $b$ , from it we get back the equation (C).

In this way we obtain by putting successively  $k = 1, 2, \dots, b - 1$  a set of  $b - 1$  equations, from which we find in the shape of determinants finite values for the  $b - 1$  quantities  $T_{b,h}$ .

Actually we have got more equations than were wanted, for we may separate real and imaginary parts.

We put

$$x - [x] - \frac{1}{2} = P(x),$$

so that  $P(x)$  stands for the fractional part of the number  $x$  minus  $\frac{1}{2}$ . Now we have generally

$$\log (1 - e^{2\pi i x}) = \frac{1}{2} \log 4 \sin^2 \pi x + i \pi P(x),$$

hence instead of (E) we get the two equations

$$\sum_{h=1}^{h=b-1} T_{b,h} \times \log 4 \sin^2 \pi \frac{hk}{b} = -2 \cos 2 \pi \frac{k}{b} + 2 \frac{\mu(b)}{\varphi(b)}, \quad (F)$$

and

$$\sum_{h=1}^{h=b-1} T_{b,h} \times P\left(\frac{hk}{b}\right) = -\frac{1}{\pi} \sin 2 \pi \frac{k}{b} \dots \dots \dots (G)$$

Again the equation (F) supposes that if we have

$$\frac{k}{b} = \frac{k'}{b'}$$

no multiples of  $b'$  should be substituted for  $b$  in the summation at the lefthand side. As for the equation (G) this limitation is superfluous since the discontinuous function  $P(x)$  vanishes for integer values of  $x$ .

As the solutions of the equation (F) and (G) seem in general to present neither regularity nor symmetry, we will proceed to consider some particular cases.

In the case  $b = 2$ , we have at once

$$T_{2,0} = -\frac{1}{2} + \frac{1}{6} + \frac{1}{10} + \frac{1}{14} \dots = 0,$$

$$T_{2,1} = 1 - \frac{1}{3} - \frac{1}{5} - \frac{1}{7} - \frac{1}{11} \dots = 0.$$

Putting  $b = 3$  and substituting  $k = 1$  in (G) we find

$$-\frac{1}{6} T_{3,1} + \frac{1}{6} T_{3,2} = -\frac{\sqrt{3}}{2\pi},$$

and since

$$T_{3,1} + T_{3,2} = 0,$$

we have

$$T_{3,1} = 1 - \frac{1}{7} + \frac{1}{10} - \frac{1}{13} + \frac{1}{19} \dots = \frac{3\sqrt{3}}{2\pi},$$

$$T_{3,2} = -\frac{1}{2} - \frac{2}{5} - \frac{1}{11} + \frac{1}{14} \dots = -\frac{3\sqrt{3}}{2\pi}.$$

In the case  $b = 6$  we may apply (D). Thus we obtain relations

$$T_{6,1} + T_{6,5} = T_{2,1} = 0, \quad T_{6,3} = T_{3,0} = 0, \quad T_{6,1} + T_{6,4} = T_{3,1} = \frac{3\sqrt{3}}{2\pi}.$$

$$T_{6,2} + T_{6,4} = T_{2,0} = 0, \quad T_{6,2} + T_{6,5} = T_{3,2} = -\frac{3\sqrt{3}}{2\pi}.$$

Joining to these the equation resulting by substituting  $b = 6$ ,  $k = 1$  in (G)

$$(T_{6,1} - T_{6,5}) P\left(\frac{1}{6}\right) + (T_{6,2} - T_{6,4}) P\left(\frac{2}{6}\right) = -\frac{1}{\pi} \sin \frac{\pi}{3},$$

there follows

$$T_{6,1} = 1 - \frac{1}{7} - \frac{1}{13} - \frac{1}{19} - \frac{1}{31} \dots = -\frac{\sqrt{3}}{\pi}, \quad T_{6,2} = -\frac{1}{2} + \frac{1}{14} + \frac{1}{26} + \frac{1}{38} \dots = -\frac{\sqrt{3}}{2\pi},$$

$$T_{6,5} = -\frac{1}{5} - \frac{1}{11} - \frac{1}{17} - \frac{1}{23} \dots = -\frac{\sqrt{3}}{\pi}, \quad T_{6,4} = +\frac{1}{10} + \frac{1}{22} + \frac{1}{34} + \frac{1}{46} \dots = +\frac{\sqrt{3}}{2\pi}.$$

If we take  $b=4$ , we have by applying (D)

$$T_{4,2} = T_{2,0} = 0,$$

$$T_{4,1} + T_{4,3} = T_{2,1} = 0,$$

and by the substitution  $b=4$ ,  $k=1$  in (G)

$$T_{4,1} \times P\left(\frac{1}{4}\right) + T_{4,3} \times P\left(\frac{3}{4}\right) = -\frac{1}{\pi},$$

hence we find

$$T_{4,1} = 1 - \frac{1}{5} - \frac{1}{13} - \frac{1}{17} + \frac{1}{21} \dots = \frac{2}{\pi},$$

$$T_{4,3} = -\frac{1}{3} - \frac{1}{7} - \frac{1}{11} + \frac{1}{15} \dots = -\frac{2}{\pi}.$$

And by subtraction we obtain

$$\sum_{m=0}^{m=\infty} \left[ \frac{\mu(4m+1)}{4m+1} - \frac{\mu(4m+3)}{4m+3} \right] = \frac{4}{\pi},$$

a result which may be compared with LEIBNITZ'S theorem

$$\sum_{m=0}^{m=\infty} \left[ \frac{1}{4m+1} - \frac{1}{4m+3} \right] = \frac{\pi}{4}.$$

Lastly the series  $T_{5,k}$  can be evaluated if we substitute  $b=5$ ,  $k=1$  in (F) and  $b=5$ ,  $k=1$ ,  $k=2$  in (G). Thus we obtain

$$(T_{5,1} + T_{5,4}) \log 4 \sin^2 \frac{\pi}{5} + (T_{5,2} + T_{5,3}) \log 4 \sin^2 \frac{2\pi}{5} = -2 \cos \frac{2\pi}{5} - \frac{1}{2},$$

$$(T_{5,1} - T_{5,4}) P\left(\frac{1}{5}\right) + (T_{5,2} - T_{5,3}) P\left(\frac{2}{5}\right) = -\frac{1}{\pi} \sin^2 \frac{2\pi}{5},$$

$$(T_{5,1} - T_{5,4}) P\left(\frac{2}{5}\right) + (T_{5,2} - T_{5,3}) P\left(\frac{1}{5}\right) = -\frac{1}{\pi} \sin^2 \frac{4\pi}{5},$$

moreover we have

$$T_{5,1} + T_{5,2} + T_{5,3} + T_{5,4} = -T_{5,0} = 0.$$

Solving the four equations, the result is as follows

$$\begin{aligned}
 T_{5,1} &= 1 + \frac{1}{6} - \frac{1}{11} + \frac{1}{21} + \frac{1}{26} + \dots = \frac{1}{2\pi} (3 \sin 72^\circ + \sin 36^\circ) - \\
 &\quad - \frac{1 + 4 \cos 72^\circ}{8 \log 2 \sin 18^\circ} = + 1.128, \\
 T_{5,2} &= -\frac{1}{2} - \frac{1}{7} - \frac{1}{17} + \frac{1}{22} - \frac{1}{37} \dots = \frac{1}{2\pi} (\sin 72^\circ - 3 \sin 36^\circ) + \\
 &\quad + \frac{1 + 4 \cos 72^\circ}{8 \log 2 \sin 18^\circ} = - 0.710 \\
 T_{5,3} &= -\frac{1}{3} - \frac{1}{13} - \frac{1}{23} + \frac{1}{33} + \frac{1}{38} \dots = \frac{1}{2\pi} (-\sin 72^\circ + 3 \sin 36^\circ) + \\
 &\quad + \frac{1 + 4 \cos 72^\circ}{8 \log 2 \sin 18^\circ} = - 0.452, \\
 T_{5,4} &= +\frac{1}{14} - \frac{1}{19} - \frac{1}{29} + \frac{1}{34} + \frac{1}{39} \dots = \frac{1}{2\pi} (-3 \sin 72^\circ - \sin 36^\circ) - \\
 &\quad - \frac{1 + 4 \cos 72^\circ}{8 \log 2 \sin 18^\circ} = + 0.034.
 \end{aligned}$$

As a numerical test I have directly calculated  $T_{5,h}^{100}$ . The results were respectively: +1.123, -0.685, -0.449, +0.036.

From these few particular cases it will be evident that the equations (F) and (G) always permit to evaluate  $T_{b,h}$  and the fact that such a series has in all cases a finite sum may with more or less justice be interpreted thus: Among the integers without quadratic factors less than a given large number  $g$ , that are solutions of a given congruence

$$x \equiv h \dots \pmod{b}$$

the integers made up by an odd number of prime factors are sensibly equal in number to the integers made up by an even number of prime factors.

**Botany.** — "*The Ascus-form of Aspergillus fumigatus Fresenius*".

By Dr. G. GRUJNS. (Communicated by Prof. F. A. F. C. WENT.)

While during the last course I was occupied with determining fungi in the botanical laboratory under the superintendence of Prof. WENT, I noticed that in a pure culture of *Aspergillus fumigatus*, a couple of months old, sporefruits had formed; on inoculation from this culture these same bodies were always produced in the new cultures.

As nutrient substance I used KONING'S malt-canesugar-agar-agar.

The ascus-form of *Aspergillus fumigatus* has not yet been described, for the statements of BEHRENS and SIEBENMANN are justly doubted by WEHMER, nor do they agree with my result.

The conidiophores agree so well with WEHMER's description<sup>1)</sup> and with his picture, also with regard to dimensions, that the diagnosis need not be doubted.

The fruit-bodies appear as small globules having the colour of fresh hazelnuts; their size is only about  $\frac{1}{4}$  mm. With feeble magnification they appear to be enclosed by an envelope of small, round, highly refractive, greenish globules, enclosing a dark body. The globules on stronger magnification turn out to be mycelium cells with a greatly thickened wall, which remain joined by a few thin threads. The body within is little transparent, deep red and irregularly egg-shaped. It has a thin fragile wall, consisting of two layers of flat cells in which a red pigment is found.

The space within is filled up with a dense web of colourless hyphae, the contents of which are homogeneous and between which the asci are found.

These are egg-shaped and have a very thin wall, which in mature asci is difficult to observe, but which can easily be recognised in immature ones still containing colourless spores.

The mature spores, of which eight are found in each ascus, have a deep red colour, which is turned blue by alkali (ammonia). They have the shape of convex lenses, the thickness of which differs only little from the diameter. Round the aequator a hyaline seam is found, showing fine radial striae or folds.

The perithecia consequently resemble those of *Aspergillus nidulans* which differs, however, by wanting the ramified sterigmata. Also the ascospores with their radially striated seam are different from those of *nidulans* which show a groove.

### Terrestrial magnetism. — "*The daily field of magnetic disturbance.*"

By W. VAN BEMMELEN. (Communicated by Dr. J. P. VAN DER STOK).

In 1895 I published<sup>2)</sup> the results of a research on the change in magnetic force on days following large magnetic disturbances.

By comparing the mean daily force on a day directly following a disturbance with the force some days after, a differential vector was obtained directed chiefly South with a deflection to West or East of rather constant azimuth for each station.

<sup>1)</sup> C. WEHMER. Die Pilzgattung *Aspergillus*, Genève 1901. p. 71.

<sup>2)</sup> Meteorologische Zeitschr. 1895, pg. 321.

Later considerations <sup>1)</sup> brought me to the result that the regular part of the disturbance phenomenon might be ascribed to the existence of a circular system of electric currents chiefly in the higher layers of the atmosphere, compassing the earth, and parallel to the lines of equal frequency of aurora borealis.

Considering with SCHMIDT <sup>2)</sup> magnetic disturbances to be caused by movement of smaller current-rings over the surface of the earth, the whole exhibits a strong analogy to the great cyclonic movement of atmospheric air around the poles and the wandering depressions within it, so as it has recently been described by H. HILDEBRANDSSON. It seemed evident that such a system of circular currents must undergo a daily fluctuation caused by the rotation of the earth and I tried to separate this influence by taking the difference of corresponding *hourly* values on days following a magnetic disturbance.

Though the results pointed to an influence indeed, they were too vague to lead to definite conclusions; the minuteness of this daily fluctuation as compared with the irregular changes accompanying magnetic disturbance being no doubt the cause of it.

Now in 1899 Dr. LÜDELING <sup>3)</sup> showed that sharp results were to be obtained, when comparing the hourly values of the horizontal components on quiet days (Normaltage) with those for all days. In his interesting paper he gives the hourly values of the horizontal components ( $v_s$  and  $\gamma_s$ ) of disturbing force for the arctic stations for the months June and July 1883.

The vectordiagrams drawn by him show the remarkable fact that the vector for all stations moves anticlockwise, with the only exception of that for the station Kingua Fjord where the vector moves decidedly in a clockwise direction. Also at Godthaab during part of the day the same occurs.

In order to study these diagrams for other parts of the earth I computed them for Greenwich, Washington, Tiflis, Zi-Ka-Wei, Batavia, South Georgia and Cape Hoorn for the same months (June, July); also deriving on the same principles the vertical component for these latter stations and the arctic ones, I found this component to exhibit chiefly a single daily fluctuation of an amount of the same order as that found for the horizontal component.

It was easy to classify the stations in the following groups:

<sup>1)</sup> Terrestrial Magnetism V, pg. 123.

<sup>2)</sup> Meteorologische Zeitschrift 1899, pg. 385.

<sup>3)</sup> Terrestrial Magnetism IV, pg. 245.

Station	Hor. vector moves in diagram :	Vertical component shows:	
		Max.	Min.
Kingua Fjord Godthaab	clockwise  anticlockwise, but clockwise in the evening.	Evening	Morning
Cape Thordsen Jan Mayen Ssagastyr Fort Rae Point Barrow Nova Zembla Bossekop	} anticlockwise.	Evening	Morning
Sodankylä		anticlockwise, but clockwise in the morning. The E/W compon. tends to disappear.	Evening
Pawlowsk Greenwich	} clockwise	Morning	Evening
Tiflis Washington		clockwise, but anticlockwise in the evening.	Morning
Zi-Ka-Wei	No change in direction, which stays WSW-ENE.	Morning	Evening
Batavia	anticlockwise, but clockwise in the evening	Noon	Morning
South Georgia Cape Hoorn	} clockwise	Morning	Evening

The change in the sense of rotation of the horizontal vector and in the times of occurrence of maximum and minimum of the vertical component proceeds quite regularly, when classifying the stations, as has been done here, by their distance from a pole, which may be called pole of aurora borealis and is located in  $\pm 80^{\circ}.5$  N and  $\pm 80^{\circ}$  W.

Now it is remarkable that in my paper on the "Erdmagnetische Nachstörung", quoted above, I came to the result, that the disturbing force acts in planes, which cut the surface of the earth along curves converging into this pole.

In order to study the behaviour of the horizontal component the

simultaneous horizontal vectors for the arctic stations (after the data given by LÜDELING) have been plotted in a series of 12 maps corresponding to the hours of  $0^h$ ,  $2^h$ ,  $4^h$  . . . .  $22^h$  mean Göttingen time. These maps revealed the fact that one part of these vectors pointed to one focus and the rest emanated from another.

The successive places of these foci have been determined as unbiased as possible. Rectangular coördinates have been made use of with the origin in the north pole and taking for  $x$  and  $y$  axis the meridians  $180^\circ$  and  $90^\circ$  E from Greenwich. The unity for the values of the coordinates as given underneath is  $2 \log 0^\circ.5$ ; accordingly the value of  $\sqrt{x^2+y^2}$  represents nearly the polar distance in degrees, because the maps have been drawn in stereographic projection. The focus to which the vectors point has been called a positive focus, that from which they emanate a negative focus.

Mean Göttingen hour	Positive focus		Negative focus	
	$x$ .	$y$ .	$x$ .	$y$ .
$0^h$	7.4	—22.2	— 8.2	1.6
2	9.6	—17.0	—13.2	— 5.4
4	11.2	—11.0	—13.2	— 8.8
6	11.2	— 6.2	—16.0	—11.6
8	8.8	2.2	—12.6	—21.2
10	0.0	2.2	— 8.8	—28.0
Noon	— 4.4	2.2	2.2	—23.6
14	— 8.8	— 0.6	8.8	—23.6
16	—11.8	— 6.6	13.8	—10.4
18	—14.0	—15.4	9.4	— 6.0
20	—13.2	—26.2	2.8	8.2
22	— 8.8	—30.2	— 6.2	6.2
Mean	— 1.1	—10.7	— 3.4	—10.2

Harmonic formulae calculated for these four series :

$$\begin{aligned}
 + \text{ focus } & \begin{cases} x = -1.1 + 13.5 \sin(t + 15^\circ) + 2.1 \sin 2(t + 19^\circ) \\ y = -10.7 + 14.3 \sin(t + 14^\circ - 90^\circ) + 2.4 \sin 2(t - 2^\circ) \end{cases} \\
 - \text{ focus } & \begin{cases} x = -3.4 + 13.6 \sin(t + 24^\circ + 180^\circ) + 3.2 \sin 2(t - 15^\circ) \\ y = -10.2 + 15.7 \sin(t + 24^\circ + 90^\circ) + 3.0 \sin 2(t - 50^\circ) \end{cases}
 \end{aligned}$$

From the constants of these formulae it follows evidently, that both foci move in nearly the same circular path with almost constant velocity and with a mutual distance of  $180^\circ$ .

This being granted and calling  $x_0$  the mean of the  $x$ 's for positive

and negative focus:  $x_0 = \frac{-1.1-3.4}{2} = -2.3$ , and  $y_0$  the mean for the  $y$ 's for the foci:  $y_0 = \frac{-10.7-10.2}{2} = -10.5$ , the values of

$(x_{0h}-x_0)$ ,  $-(x_{12h}-x_0)$ ,  $(y_{0h}-y_0)$  and  $(-y_{18h}-y_0)$  and so on, must represent the same quantity, from which we may compute a set of 12 means. The harmonic formulae representing this set is:

$$x_+ = -2.3 + 14.5 \sin(x + 22^\circ) + 1.3 \sin 2(x + 28^\circ).$$

The term of the second order, already small in comparison with that of the first order, having been still more diminished by this operation, it may be safely neglected. So we may adopt (for Greenwich time):

$$x_+ = -2.3 + 14.5 \sin(x + 12^\circ)$$

$$y_+ = -10.5 + 14.5 \sin(x + 12^\circ - 90^\circ).$$

The centre of the circular path, which is best called "pole of disturbance" lies accordingly in

$$79^\circ \text{ N. and } 78^\circ \text{ W.}$$

For the pole of aurora borealis I accepted

$$80^\circ.5 \text{ N. and } 80^\circ \text{ W.}$$

and according to SCHMIDT the magnetic axis for 1885 cuts the surface in

$$78^\circ.5 \text{ N. and } 68^\circ.5 \text{ W.}$$

So we have arrived at the remarkable result, *that the daily movement of the arctic foci of disturbing force takes place in a circular path of  $14^\circ.5$  radius around a pole practically coinciding with the pole of aurora borealis and lying very near to the north end of the magnetic axis.*

When now supposing this fluctuation of disturbing force to be caused by a field, which slides around the earth from East to West (as has already been remarked by LÜDELING in his paper quoted above) and this in analogy with our actual views regarding the field of the ordinary daily variation, we are obliged to assume the field of disturbance to revolve around the axis just found, viz.

$$78^\circ \text{ N. } 79^\circ \text{ W. to } 78^\circ \text{ S. } 101^\circ \text{ E.}$$

In order to represent the daily field, we have to study the vector-diagrams themselves. Of course the vector-diagrams of one group show mutual differences caused partly by insufficient material (for the arctic stations 2 or 3 months only) and partly by local influences, as has already been indicated by SCHMIDT (Met. Z. 1899).

In order to avoid irregularities bringing confusion in the result, which may prevent interpretation of this phenomenon (this being of

course the principal aim), I have chosen as representative for each group one station with an obviously regular diagram.

They are: Kingua Fjord, Jan Mayen, Sodankylä, Greenwich, Tiflis, Zi-Ka-Wei, Batavia, Cape Hoorn, (Godthaab has been left out, it being rather superfluous for the horizontal component, and the vertical component not being available).

The values of the components have been graphically smoothed. Now to obtain a representation of the daily field the method at present common of distributing the successive hourly values for each station along the parallel of that station, has been applied, and thus I have constructed a map in MERCATOR'S projection *but according to the axis of disturbance* with the lines of equal vertical component and horizontal vectors on it.

The lines of equal vertical component compass chiefly eight foci of maximum and minimum vertical force (of which two are double), tabulated hereafter. (It should be kept in mind, that latitudes and longitudes are according to the axis of disturbance). The longitude of the sun for its position on June 21<sup>st</sup> has been taken zero.

Latitude	Longitude	Amount	Latitude	Longitude	Amount
71°	161° W	-47 $\gamma$	} 77°	6 E	+ 57 $\gamma$
				} 71°	81 E
} 52	156 W	+ 7	} 52		88 E
	131 W	+ 7		} 22	129 E
-10	41 W	+ 3	} South of -60		? E
South of -60	? W	- ?			

*The horizontal vectors drawn in the same map are pointing almost without exception towards the positive foci and away from the negative ones.*

Supposing the disturbing force to originate from existing electric currents, the fact that these currents must follow nearly the course of the lines of equal vertical force conduces to the hypothesis of systems of circular currents with eight foci revolving daily around the axis of disturbance.

The horizontal vector being directed to the point where the vertical component is upwards, the application of AMPÈRE'S rule teaches that these currents must flow for the greater part above the surface of the earth.

Remarkable is the rapid diminution of the force with the polar distance, almost parallel to the equally rapid diminution in the occurrence of auroral display. I must emphasize an important divergence between the fields of ordinary daily variation and that

of disturbance; viz. the former has its foci near the meridians of noon and midnight, the latter near the line of separation of day and night.

The axis around which the field of disturbance revolves is so nearly coincident with the magnetic axis of the earth, that it seems the field is caused by any emanation from the sun, deflected by the earth-magnet acting as a whole, and not by the surface distribution of terrestrial magnetic force.

Full account on this research will be soon given in the *Natuurkundig Tijdschrift voor Nederlandsch-Indië*.

**Geology.** — “*A piece of Lime-stone of the ceratopyge-zone from the Dutch Diluvium.*” By J. H. BONNEMA (Communicated by Prof. MARTIN).

In a few papers which a short time ago appeared in these reports, I communicated some particulars of the Cambrian erratic blocks from the loam-pit near Hemelum; this time I intend to treat of the Under-silurian ones.

First of all, however, I wish to add something to my information concerning the way in which Under-cambrian sandstone with *Discinella Holsti* MOBERG is spread. I then <sup>1)</sup> said that I had not been able to find anything certain, in German literature, about erratic-blocks of this stone. This was a consequence of my sources of information on sedimentary erratic-blocks being incomplete. After my paper had appeared, Prof. STOLLEY <sup>2)</sup> was so kind as to send me an essay that had seen the light already a few years before, in which the occurrence of this kind of erratic-blocks in the German diluvium is made mention of.

No more did I find, here in the Hemelum loam-pit, the opinion confirmed expressed i. a. by STARING <sup>3)</sup>, MARTIN <sup>4)</sup> and SCHROEDER VAN DER KOLK <sup>5)</sup>, that Under-silurian erratic-blocks were almost entirely

<sup>1)</sup> BONNEMA, Some new Under-cambrian erratic-blocks from the Dutch Diluvium. Proc. Royal Acad. Amsterdam. Vol. V (1903) p. 561.

<sup>2)</sup> STOLLEY, Einige neue Sedimentärgeschiebe aus Schleswig-Holstein und benachbarten Gebieten. Schriften des Naturwissenschaftlichen Vereins für Schleswig-Holstein. 1898. Bd. XI. p. 133.

<sup>3)</sup> STARING, De bodem van Nederland. 1860. II. p. 99.

<sup>4)</sup> MARTIN, Niederländische und Nordwestdeutsche Sedimentärgeschiebe. 1878. p. 14.

<sup>5)</sup> SCHROEDER VAN DER KOLK, Bijdrage tot de kennis der verspreiding onzer kristallijne zwerfelingen. Dissertatie. 1891. p. 51. Stelling VII.

absent in our diluvium. With regard to Groningen this was already told us by VAN CALKER<sup>1)</sup>. Afterwards I pointed out the same thing for Kloosterholt<sup>2)</sup>, and it will appear, too, that boulder-clay of Hemelum contains as many Under-silurian erratic-blocks as the loam of the places mentioned.

That the above-named writers are of different opinions may be easily explained by the way in which stones used to be gathered. Formerly the hammer was hardly ever used and there is no doubt that only those stones were gathered whose outward appearance drew the attention. Now, this very rarely happens with Under-silurian erratics. The polyparia of *syringophyllum organum* L., which are probably without any exception Under-silurian, are conspicuous for their form, and we really see that old collections contain these fossils in large numbers. The Upper-silurian erratics, however, on the outside of which it is sometimes already visible that they are rich in fossils (which is i. a. the case with limestones with *chonetes striatella* Dalm), much sooner draw the attention. This is especially the case with petrified corals, which mostly have an Upper-silurian age. They form, indeed, the greater part of the old collections.

Even if one uses a hammer while gathering stones, one is sure to find, in proportion, more Upper-Silurian erratics with determinable fossils than Under-Silurian ones, because as a rule the former are much richer in fossils than the latter.

Moreover, in Upper-Silurian erratics *Leperditia*-valves are frequently found. As, in consequence of their comparatively small size and their smooth surface, these valves are easily exposed to view and the different kinds of *Leperditia* are easily distinguished and are characteristic of different strata, one may, by means of these remains, determine the age of many Upper-Silurian erratics.

A great part of our Under-Silurian erratics, however, consist of pieces of tough, greyish lime-stone, which does not possess many petrifications, so that these pieces seldom give a determinable fossil. Very often an *Asaphus*, an *Illaenus* or an *Endoceras*, found in them, proves their Under-Silurian age, whereas these remains are too incomplete to allow of their being ranged under a definite division of Under-Silurian erratics.

This is even more the case with that kind of limestone of frequent

<sup>1)</sup> VAN CALKER, Ueber das Vorkommen cambrischer und untersilurischer Geschiebe bei Groningen. Zeitschr. d. deutsch. geol. Gesellschaft. Bd. XLIII. pag. 792.

<sup>2)</sup> BONNEMA, De sedimentaire zwerfblokken van KLOOSTERHOLT. Versl. v. d. Koninkl. Akad. v. Wetenschappen. 1898. pag. 448.

occurrence, which petrographically resembles the lithographical one and probably is of the same age as the Wesenbergen stratum. In this stone a petrification is hardly ever found.

Consequently it takes a long time to gather a collection in which the different divisions of Under-Silurian stone are clearly represented. I did not succeed in composing such a collection from the Hemelum loam-pit. This is partly owing to the fact that this opportunity to gather erratics existed only a short time. The boulder clay proving unfit for use in brick-works, digging has been left off.

The principal cause is, however, that boulder clay used to be dug there in the beginning of winter, and that in the latter part of that season the erratics found were broken to pieces for macadamizing roads, whilst in this very part of the year neither my occupations nor the weather allow of my making excursions.

The erratic I am going to treat of, was found by me in the Hemelum loampit a few years ago; it may undoubtedly be ranged under the *Ceratopyge*-zone, the eldest of the Under-Silurian kinds.

It contained a kernel of compact, splintery limestone, of a light-grey, more or less greenish colour. This kernel was surrounded by a yellow-brown, softer crust, caused by corrosion, which was coloured greyish at the surface. Occasionally I distinguished small glauconite- and pyrite-grains.

When I broke it to pieces, the kernel naturally did not give me any fossils; I succeeded, however, in exposing to view, from the corrosion-crust, the following fossils:

1. *Ceratopyge forficula* Sars<sup>1)</sup>. Of this species I found a head-midshell, a free cheek and three fragments of pygidium. These remains come from the variety *acicularis* Sars et Boeck, the axis of the pygidium consisting of 6 segments. The head-midshell, too, bears more resemblance to fig. 15 than to fig. 17.

2. *Symphysurus angustatus* Sars et Boeck<sup>2)</sup>. One glabella and three small pygidia were found. In the latter it becomes quite clear that as a rule the axis may be clearly distinguished only in stone-kernels.

3. *Holometopus* (?) *elatifrons* Ang<sup>3)</sup>. Numerous more or less uninjured head-midshells presented themselves. Only in one specimen, one side of which is still in the stone, the prick in which the glabella ends towards the back is visible.

<sup>1)</sup> BRÖGGER, Die silurischen Etagen 2 und 3. p. 123. Tab. III. fig. 15—22.

<sup>2)</sup> BRÖGGER loc. cit. p. 60. Tab. III. fig. 9, 10, 11.

<sup>3)</sup> BRÖGGER loc. cit. p. 128. Tab. III. fig. 13.

4. *Euloma ornatum* Ang<sup>1)</sup>. A piece of a head-midshell and of a pygidium were exposed to view.

5. *Agnostus Sidenbladhi* Linnr.<sup>2)</sup>. This species is represented by a head-shell.

6. *Shumardia pusilla* Sars<sup>3)</sup>? I am inclined to range under this head a very small pygidium, which doubtless comes from a Shumardia-species. That I am not quite certain here, is owing to the fact that it shows a lateral compression and consequently is not so broad as the pygidium pictured by Moberg<sup>4)</sup>. The latter, which has been produced from slate, may be somewhat flattened, whereas the pygidium out of my erratic-block has probably retained its original shape. It is also possible, however, that it comes from a new Shumardia-species. According to Hennig<sup>5)</sup> such a new species is met with in the Ceratopyge-zone of Fågelsång. Unfortunately the essay in which this species was to be described — which essay was shortly to be published, according to that writer —, still keeps us waiting.

7. *Orthis Christianiae* Kjerulf<sup>6)</sup>. Several valves of this little Brachiopode were found.

The three first species of Trilobites are, according to Tullberg<sup>7)</sup> also met with in the lowest strata of Oeland Orthocere-lime, but as this does not appear to be the case with the other fossils, I do not hesitate to call this erratic-block a piece of Ceratopyge-lime.

Erratic-blocks from the Ceratopyge-zone with remains of Trilobites seem to be very rare in the German and the Dutch diluvium. As far as I can see, only two have been made mention of by Remelé<sup>8)</sup> and one by Stolley<sup>9)</sup>, as most certainly belonging to this zone.

1) Brögger loc. cit. p. 97. Tab. III. fig. 5, 6.

2) Linnarsson, Om Vestergotlands cambriska och siluriska aflagringa. Svenska Vetenskaps-Akademiens handlingar. 1869. Bd. 8 No. 2. p. 74. Tab. II. fig 33, 34.

3) Brögger, loc. cit. p. 125. Tab. XII. fig. 9.

4) Moberg, Om en afdelning inom Oelands Dietyonema-skiffer s'som motsvarighet till Ceratopygeskiffern i Norge. Sveriges geologiska undersökning. Ser. C. No. 109. p. 4.

5) Hennig, Geologischer Führer durch Schonen. 1900. p. 33.

6) Gagel, Die Brachiopoden der Cambrischen und Silurischen Geschiebe im Diluvium der Provinzen Ost- und Westpreussen. Beiträge zur Naturkunde Preussens, herausgegeben von der Physikalisch-Oeconomischen Gesellschaft zu Königsberg. No. 6. 1890. p. 34. Taf. II. fig. 22.

7) Tullberg, Förelöpande redogörelse för geologiska resor på Oeland. Geologiska Föreningens i Stockholm Förhandlingar. 1882. Bd. VI. p. 231.

8) Remelé, Ueber das Vorkommen des Schwedischen Ceratopyge-kalks unter den Norddeutschen Diluvialgeschieben. Zeitschr. d. deutschen geol. Gesellschaft 1881. Bd. 33. p. 696.

9) Stolley, loc. cit. p. 135.

They are, however, not like the Hemelum piece, those of REMELÉ being many-coloured and that of STOLLEY being a piece of yellow iron-ochre, which according to him probably originates, through the influence of corrosion, from a clayish kind of stone, which is rich in iron.

Formerly REMELÉ<sup>1)</sup> declared that the erratic-block found near Neustrelitz, from which BEYRICH described his *Harpides rugosus*, most probably was Ceratopyge-lime. He came to this conclusion especially because in the Swedish and Norwegian Ceratopyge-zones is found the species that is the nearest relation to *Harpides rugosus* Sars et Boeck, and that at the time no specimen of this species had been found in higher strata.

Now that TULLBERG<sup>2)</sup> has informed us, however, that in the lowest, grey Orthoceratite-lime of Oeland a new species of *Harpides* is found, this erratic-block is much less likely to be Ceratopyge-lime. The less so, as according to REMELÉ this erratic greatly resembles glauconite Vaginaten-lime (= lowest grey Orthoceratite-lime).

If attention is paid only to the petrographical nature and the presence of *Orthis Christinia*, most probably more erratics of the same kind have been found in the German diluvium. GOTTSCHÉ<sup>3)</sup> at least makes mention of a light-grey, splintery lime-stone, green- and yellow-tinted, which LUNDBERG took for Ceratopyge-lime. He also tells us, however, that this stone perfectly resembles pieces of Ceratopyge-lime that were gathered by DAMES near Aeeklinta, whereas HOLM<sup>4)</sup> informs us that this Under-silurian zone is entirely absent there.

It is possible, too, that to this kind belongs the Ceratopyge-lime which STEUSSLOFF<sup>5)</sup> under *b* described as light-grey lime with a greenish tint and a little *Orthis*.

Corresponding erratics seem also to have been found by STOLLEY<sup>6)</sup>.

1) REMELÉ, loc. cit. p. 500, 695.

2) TULLBERG, loc. cit. p. 232.

3) GOTTSCHÉ, Die Sedimentär-Geschiebe der Provinz Schleswig-Holstein. 1883. p. 14.

4) HOLM, Om de vigtigaste resultaten från en sommaren 1882 utförd geologisk-palaeontologisk resa på Oeland. Öfversigt of Kongl. Vetenskaps Akademiens Förhandlingar. 1883. p. 67.

5) STEUSSLOFF, Sedimentärgeschiebe von Neubrandenburg. Archiv des Vereins der Freunde der Naturgeschichte in Mecklenburg. 1892. p. 163.

6) STOLLEY, Die cambrischen und silurischen Geschiebe Schleswig-Holsteins und ihre Brachiopodenfauna. Archiv für Anthropologie und Geologie Schleswig-Holsteins und der benachbarten Gebiete. 1895. Bd. I. p. 43.

Only those pieces are considered which, as he says, are so compact as to resemble serpentine.

An erratic-block of the same kind has perhaps also been found in the eastern part of the German diluvium. GAGEL<sup>1)</sup> at least speaks of a greenish, hard piece of limestone, with yellow spots here and there in consequence of corrosion, in which little glauconite-grains occur rather scattered. He does not tell us whether it is compact.

Though in all these pieces, except that of STEUSSLOFF, *Orthis Christianiae* is declared to be present, and though petrographically they seem more or less to resemble my erratic-block, — I dare not take it for granted that they are closely related to it.

It must further be traced where corresponding limestone is still found as firm rock. This is certainly the case at Ottenby on the western coast of the southernmost part of Oeland. Last summer I could convince myself of this. Ceratopyge-lime is there not only of the same petrographical nature (in most cases at least), but is also rich in fossils. HOLM informs us that towards the midst of the island this stratum is less developed; its colour is more reddish here, and it is less rich in fossils, so that as a rule only *Orthis Christianiae* is met with. In the northern part of Oeland it is altogether absent, according to HOLM.

In Schonen, Ceratopyge-lime has been found only near Fågelsång, as far as one knows for certain. This kind, however, is more bluish-coloured, which I can observe in a piece I received from Prof. MÖBERG. Corresponding limestone may also occur in West-Gotland, on Kinnekulle and Hunneberg. According to LINNARSSON<sup>2)</sup> the Kinnekulle-stone is a hard, light-grey, mostly bluish and greenish limestone, often with numerous small, blackish-green glauconite-grains. He says that the Hunneberg limestone is little or not at all bituminous, now compact, now crystalline, either black or grey, and frequently containing pyrite. So there is a possibility, to be sure, that such-like limestone is found there; but without any material for comparison nothing can be said with certainty.

Ceratopyge-lime, which, as is generally known, is not met with in the Russian Baltic-seaprovinces, moreover still occurs as firm rock in the south of Norway and in the environs of Christiania and Mjösen. HOLM<sup>3)</sup> declares it to be occasionally so much like that of Ottenby in Oeland, that he is unable to distinguish one kind from

<sup>1)</sup> GAGEL, loc. cit. p. 9. 1b.

<sup>2)</sup> LINNARSSON, loc. cit. p. 30, 56.

<sup>3)</sup> HOLM, loc. cit.

the other. BRÜGGER<sup>1)</sup>, however, tells us again and again that it is blue-coloured, so that I suppose that in colour it more resembles that of Fågelsång. A piece of Ceratopyge-lime which I saw at the Groningen Geological Institute, seems to confirm this opinion.

Finally it remains to be examined where we must look for the origin of this erratic-block. I suppose it to come from a place not far from Ottenby. The in every respect perfect resemblance between our erratic and Ceratopyge-lime that is found there, may first of all be said to speak in favour of this opinion. The circumstance, secondly, that in the Hemelum loampit I found many kinds of erratic-blocks that are also found in Oeland, makes this highly probable. I need only remind of those pieces which I formerly described, pieces of Scolithus-sandstone, sandstone with intersecting layers and Discinella Holsti-sandstone; whilst there are many more, as I hope I shall point out within a short time. This resemblance in erratic-blocks makes it more probable, first that the ice came down to us via those regions, and at the same time that a piece of Ceratopyge-lime was brought from there to here.

**Chemistry.** — In the meeting of Saturday May 30, 1903 Prof. S. HOOGWERFF and Dr. W. A. VAN DORP communicated a paper: "*On the compounds of unsaturated ketones with acids*" and in the meeting of Saturday September 26, 1903 Prof. TH. H. BEHRENS communicated a paper: "*The conduct of vegetal and animal fibers towards coal-tar-colours*".

(Both communications will not be published in these Proceedings).

<sup>1)</sup> BRÜGGER, loc. cit. p. 14.



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday November 28, 1903.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 28 November 1903, Dl. XII).

C O N T E N T S.

- A. F. HOLLEMAN and J. W. BEEKMAN: "Benzene fluoride and some of its derivations", p. 327.  
H. W. BAKHUIS ROOZEBOOM: "The system Bromine + Iodine", p. 331.  
R. O. HERZOG: "On the action of emulsin". (Communicated by Prof. C. A. PEKELHARING), p. 332.  
EUG. DUBOIS: "Deep boulder-clay beds of a latter glacial period in North-Holland". (Communicated by Prof. K. MARTIN), p. 340.  
G. VAN RIJNBERK: "On the fact of sensible skin-areas dying away in a centripetal direction" (Communicated by Prof. C. WINKLER), p. 346.  
C. WINKLER and G. VAN RIJNBERK: "Structure and function of the trunk-dermatoma", IV, p. 347.  
J. D. VAN DER WAALS: "On the equilibrium between a solid body and a fluid phase, especially in the neighbourhood of the critical state", (II part), p. 357.  
P. H. SCHOUTE: "Centric decomposition of polytopes" p. 366.  
J. M. VAN BEMMELEN: "Absorption-compounds which may change into chemical compounds or solutions", p. 368.

The following papers were read:

**Chemistry.** — "*Benzene fluoride and some of its derivations.*" By  
Prof. A. F. HOLLEMAN and Dr. J. W. BEEKMAN.

(Communicated in the meeting of September 26, 1903).

Benzene fluoride has, up to the present, been a not at all readily accessible substance. The best known method of preparation is that of WALLACH and HEUSLER (A. **245**, 255) which consists in first preparing benzenediazopiperidide and decomposing this with

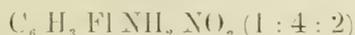
hydrogen fluoride. These chemists are even of opinion that benzene fluoride may thus be readily prepared by the kilo. As regards the course of the reaction our experiences are quite in harmony with those of WALLACH and HEUSLER, but we differ in the appreciation of the convenience of the method. Apart from the fact that in our numerous experiments we have never succeeded in obtaining the yield of 50% (on an average we only got 30% from the aniline employed) which they claim to obtain, the recovery of the piperidine proved to be very tedious. Notwithstanding its price is considerably lower than it used to be, as it is now prepared by electrolytic reduction of pyridine, it is still such that this recovery could not be avoided. The base must be again isolated in a state of perfect purity, because the yield of diazopiperidide becomes very small if the smallest impurity should be present. The method is also very tedious as not more than 10 grams of diazopiperidide at a time should be treated with hydrofluoric acid, otherwise the reaction becoming too violent. After having prepared about 150 grams of benzene fluoride in this way we, therefore, decided to abandon this method and to endeavour to obtain benzene fluoride by the direct diazotation of aniline.

For this purpose VALENTINER and SCHWARTZ have taken out a patent (Centralblatt 1898 I, 1224) consisting in heating a solution of benzenediazonium chloride with hydrogen fluoride. We may surmise that the product will be a benzene fluoride contaminated with benzene chloride; on following their directions this proved to be the case to such an extent that after repeated fractionation of the product 100 grams of aniline yielded only two grams of fairly pure benzene fluoride. This showed that in the diazotation of aniline, intended for the preparation of benzene fluoride hydrochloric acid should be avoided.

I do not wish to enter into particulars as to the various ways in which we have tried to prepare benzene fluoride directly from aniline. Dr. BECKMAN has stated something about this in his dissertation. It will be sufficient to mention here that the yield of the desired product increased with the amount of hydrofluoric acid employed. This is the method which we finally adopted: 93 grams of aniline are dissolved in sulphuric acid and diazotated in the usual manner, care being taken that the volume of liquid does not exceed 1.25 litre. The ice-cold solution is then poured slowly with vigorous stirring into a copper vessel containing 500 cc. of 55% hydrofluoric acid heated nearly to the boiling point and kept at that temperature. The benzene fluoride distills over and is condensed in a leaden worm-condenser surrounded by ice and salt. The distillate consists of a colorless liquid, which is freed from traces of phenol

by washing with a little alkali. After drying over calcium chloride it at once distilled over at a constant temperature of 85°. From 93 grams of aniline 37 grams of benzene fluoride are thus obtained in a perfectly pure condition, that is to say 40% of that required by theory. The deficiency in the yield is caused by the formation of phenol. Probably this may be reduced to a minimum if instead of hydrofluoric acid a mixture of sulphuric acid and calcium fluoride is used in such a manner that the concentration of the hydrogen fluoride remains about constant. As this plan involves vigorous stirring and as our mechanical appliances were inadequate to stir the resulting paste of gypsum, we have not been able to practically confirm this obvious conclusion.

In quite an analogous manner the para- and metanitrobenzene fluoride may be prepared from the corresponding nitranilines and the three toluene fluorides from the toluidenes. Anthranilic acid, however, only yielded small quantities of *o*-fluorobenzoic acid and was nearly all converted into salicylic acid. It was very interesting to notice that, when treated by this process, orthonitraniline did not yield a trace of ortho-nitrobenzene fluoride but only resinous masses. WALLACH has also been unable to prepare this substance by his own method as he did not succeed in purifying the piperidine required. We have made two further attempts to prepare this substance. Firstly by isolating it from the nitration product of benzene fluoride, but as this contains but little of it we did not succeed either by freezing or by fractional distillation. Secondly from parafluoronitrobenzene: the *p*-aniline fluoride obtained by its reduction yields when nitrated in sulphuric acid solution



so that by eliminating the amido-group, *o*-nitrobenzene fluoride must be formed. But only resinous masses were again produced here.

The determination of carbon, hydrogen and nitrogen in the fluorine compounds could be done in the usual manner. For that of the fluorine we used a platinum tube 35 cm. in length and 1.8 cm. in diameter in which the substance was introduced mixed with CaO. After heating the mass contains the fluorine as calcium fluoride, which is then freed from the excess of lime by treatment with dilute acetic acid, collected on a filter and weighed. As we never found lime to be perfectly soluble in dilute acetic acid, it was purified by dissolving it in dilute acetic acid, precipitating with ammonium carbonate and igniting the carbonate so obtained.

The physical constants of some of the compounds prepared by us, were accurately determined and the following values were found:

	m. p.	b. p.	sp. gr. at 84°.48
<i>m</i> -nitrobenzene fluoride	1°.7	205°	1.2532
<i>p</i> - " " "	26°.5	205°	1.2583
<i>p</i> -aniline fluoride	—	187°	—
nitraniline fluoride(1:2:4)	98°	—	—
benzene fluoride	—41°.2	85°	1.0236 (at 20°/4)

It is a well known fact that the halogen in the halogen benzenes is very inert but that on further substitution in the benzene nucleus its displacement may be much facilitated. In how far this is the case with benzene fluoride and its derivatives has received but insufficient notice up to the present. WALLACH and HEUSLER (A. 243, 242) state that sodium acting at a gentle heat on an ethereal solution of benzene fluoride abstracts all the fluorine with formation of diphenyl. We repeated this experiment, but noticed but little formation of diphenyl although considerable quantities of resin were formed. Moreover, the sodium was but little attacked. Another process for studying the decomposition of halogen benzenes is that of LÖWENHERZ consisting in dissolving the compound in a large excess of alcohol and then adding sodium. If we call ( $Na$ ) the number of gram-atoms of sodium which is present at a given moment in a kilo of solvent,  $a$  the original halogen compound and  $x$  the portion then converted we have according to him the relation

$$\frac{dx}{d(Na)} = K(a - x)$$

in which  $K$  is a constant which he gives the name of "useful effect" (Nutzeffect).

We repeated one of LÖWENHERZ's experimental series with benzene chloride and found the useful effect to be 0.261 whereas he had found 0.254 and 0.268.

On applying the process to benzene fluoride it was found that sodium when acting on its alcoholic solution does not abstract a trace of fluorine, so that the useful effect = 0. This result is surprising, because according to the investigations of LÖWENHERZ the useful effect is about equally great for the other halogen benzenes. It shows that the fluorine in the nucleus is more firmly combined than the other halogens; some data of WALLACH and HEUSLER agree with this view, for instance, that by the action of sodium on an ethereal solution of *p*-benzene fluorobromide for 8 days a large amount of sodium bromide had separated but not a trace of Na Fl.

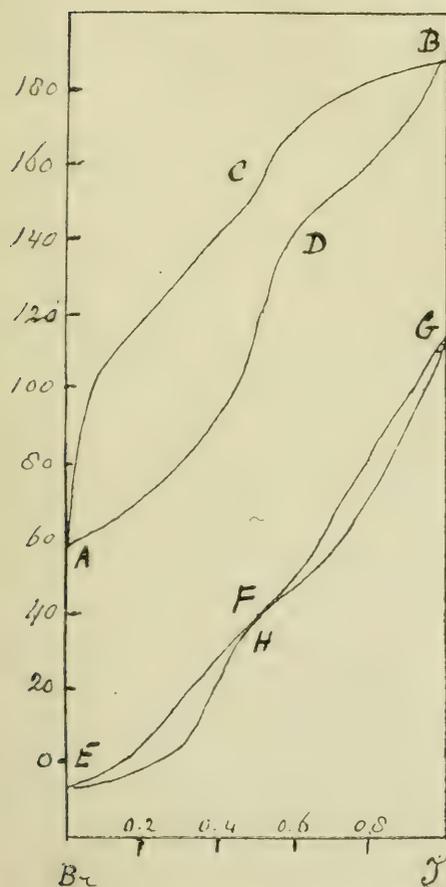
On the other hand we notice the great facility with which the fluorine of the benzene nitrofluorides reacts with sodium methylate;

the *m*- and *p*-compounds, when heated for a short time with this reagent in a methyl alcoholic solution, are quantitatively converted into the corresponding nitro-anisols. In the case of benzene dinitrofluoride (Fl.  $\text{NO}_2 : \text{NO}_2 = 1 : 2 : 4$ ) the progressive action of the sodium methylate was studied by the method employed by LILORS for the corresponding Cl-compound and it appeared that the reaction was quite completed within a few minutes. Owing to this great celerity, accurate quantitative measurements were very difficult; but it was found that the reaction constant in round numbers is 600 times larger than with the chlorine compound.

*Groningen*, Sept. 1903. Chem. Lab. University.

**Chemistry.** — “*The system Bromine + Iodine.*” By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of September 26, 1903.)



The elements chlorine and iodine yield two chemical compounds which have been accurately investigated by STORTENBEKER. Up to the present the relations of the other halogens remained in obscurity. The system Bromine and Iodine investigated by Mr. MEERUM TERWOGT gave, provisionally, the results represented in our temperature-concentration figure.

First of all the two boiling lines ADB and ACB, which were both determined at 1 Atm. pressure. The first line represents the boiling points of the series of liquid mixtures from 100% Br. to 100% I; the second line represents the vapours yielded by these mixtures. The corresponding points are situated on horizontal joining lines.

The figure shows that these curves are continuous, but

approach each other between 50 and 60% I. This case, therefore, is similar to the behaviour of the mixtures of Cl and S studied some time ago<sup>1)</sup>, with this difference that for the composition  $S_2Cl_2$  the lines nearly came into contact, whilst in this case the distance remains much greater.

The peculiar form of the boiling lines points, however, to the existence of combined molecules of the two elements. Whether these answer to the formula Br I cannot be decided from the form of this line, but perhaps better from the p,x-lines which will be studied afterwards.

Below the line ADB the region of the liquids is situated. These on further cooling deposit solid phases. These phenomena are represented by the two lines EFG and EHG. The second line shows the initial and the first line the final solidifying points. They form two continuous lines which however come into contact at 50 atom percent I.

A similar type of solidification points as a rule to mixed crystals.

The equality of the composition of liquid and solid at the concentration Br I — without this point being a maximum or a minimum — could, however, only be explained by assuming that Br I is a chemical compound.

Possibly this is the case, which has never as yet been satisfactorily proved, where a compound is mixable with both its components. We will endeavour to elucidate this matter by a determination of the density etc.

**Chemistry.** — “*On the action of emulsin.*” By Dr. R. O. HERZOG.  
(Communicated by Prof. C. A. PEKELHARING).

(Communicated in the meeting of October 31, 1903).

I. If we mix a solution of canesugar with invertin and determine the quantity inverted in definite times at a constant temperature, it appears that the inversion does not proceed as a reaction of the first order  $\left(k = \frac{1}{t} \cdot \frac{a}{a-x}\right)$ , the “constants” calculated from this equation increasing continuously during the period of the inversion. This might be explained by the increasing activity of the enzyme or by the influence exerted by the invert sugar formed.

V. HENRI<sup>2)</sup> has shown in an exhaustive paper that the latter is the cause and that the reaction proceeds according to the law

<sup>1)</sup> These Proc. June 1903.

<sup>2)</sup> Zeitschr. für physikalische Chemie **39**, 194 (1901).

regulating the unimolecular reaction where the products of reaction act (positively) autocatalytically.

For a similar case, OSTWALD<sup>1)</sup> has given the equation of reaction:

$$\frac{dx}{dt} = (k_1 + k_2 x) (a-x) \dots \dots \dots (1)$$

If we integrate this equation and take  $x = 0, t = 0$  we find:

$$\frac{1}{k_1 + k_2 a} \cdot l \cdot \frac{a(k_2 x + k_1)}{k_1(a-x)} = t \dots \dots \dots (2)$$

In this equation  $a$  is the concentration at the beginning,  $x$  the amount of sugar inverted at the period  $t$ ,  $k_1$  and  $k_2$  are the velocity constants. If we call

$$\frac{ak_2}{k_1} = \epsilon \dots \dots \dots (3)$$

we obtain the expression

$$k_2 = \frac{1}{t(1+\epsilon)} \cdot l \cdot \frac{a+\epsilon x}{a-x} \dots \dots \dots (4)$$

which is more convenient for purposes of calculation.

In this particular case  $\epsilon = 1$ , therefore for  $a = 1$   $k_1 = k_2$ .

Equation (4) now becomes:

$$2k_2 = \frac{1}{t} \cdot l \cdot \frac{a+x}{a-x} \dots \dots \dots (5)$$

2. If we measure the velocity of the emulsin action it appears that the "constants" of the logarithmic expression keep on decreasing as has already been stated by TAMMANN<sup>2)</sup>.

As it appears from HENRI's experiments<sup>3)</sup> that the enzyme suffers no change, at least when the time of reaction is a short one, it was evident that the cause of the phenomenon was to be sought in a negative autocatalysis namely, *in the retarding influence of the products of inversion*.

In a similar case the equation of the reaction assumes, according to OSTWALD<sup>4)</sup> this form:

$$\frac{dx}{dt} = (k_1 - k_2 x) (a-x) \dots \dots \dots (6)$$

After integration and calling  $x = 0, t = 0$ , we find:

1) Lehrbuch der allgemeinen Chemie, II, 2. 1 Teil, S. 264, 265.

2) Zeitschr. für physikalische Chemie 18. p. 426 (1895).

3) Thèses P. 106, 107. (Paris 1903).

4) l.c. 271.

$$\frac{1}{k_1 - ak_2} l \cdot \frac{ak_2(k_1 - k_2, x)}{k_1(ak_2 - k_2, x)} = t \dots \dots \dots (7)$$

If again we take :

$$\frac{ak_2}{k_1} = \epsilon \dots \dots \dots (8)$$

we find :

$$l_1 = \frac{1}{t(1-\epsilon)} l \cdot \frac{a-\epsilon x}{a-x} \dots \dots \dots (9)$$

or

$$l_1(1-\epsilon) = \frac{1}{t} l \cdot \frac{1-\epsilon \frac{x}{a}}{1-\frac{x}{a}} \dots \dots \dots (10)$$

in which *a* is the concentration at the beginning, *x* the amount of sugar inverted in the period *t*, *k*<sub>1</sub> the velocity constant of the reaction if taking place without autocatalysis and *k*<sub>2</sub> the constant of the autocatalysis.

3. This formula was investigated in a number of cases and it appeared that the reaction may indeed, be represented by that expression.

As in the case of invertin it has appeared that the quantity  $\epsilon$ , which, according to the assumption made, need only remain constant during the same series of experiments, as a rule suffers but little change (from 0.6 to 0.8). Probably, the value of  $\epsilon$  depends on the previous history of the enzyme, but it should be remembered that emulsin is much more sensitive than invertin.

In the following tables

*a* stands for the concentration at the start

*x* the quantity inverted, therefore

$\frac{x}{a}$  the relative quantity inverted

*t* the corresponding time in minutes.

The third column contains the value of  $k_1(1-\epsilon)$  calculated according to (10).

In the fourth column we find  $q = \frac{1}{t} l \cdot \frac{a}{a-x}$

Experiments by V. HENRI <sup>1)</sup> on October 30, 1902

## I.

0.14 N. Salicin solution  $\varepsilon = 0.6$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^3$	$\varepsilon \times 10^3$
0.132	25	[61]	246
0.209	55	80	485
0.306	87	81	482
0.534	211	78	457
0.603	271	76	448
0.686	375	73	435
0.950	1325	75	400

## II

0.07 N. Salicin solution  $\varepsilon = 0.6$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^3$	$\varepsilon \times 10^3$
0.174	24	45	345
0.351	54	46	348
0.450	86	44	302
0.691	210	43	243
0.775	270	44	240
0.847	371	44	220

## Experiments by V. HENRI on October 8, 1902.

## I.

0.14 N. Salicin solution  $\varepsilon = 0.6$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^3$
0.110	31	[68]
0.305	123	53
0.447	211	58
0.516	276	56
0.583	343	56

## II.

0.07 N. Salicin solution  $\varepsilon = 0.6$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^3$
0.476	122	41
0.651	200	42
0.691	275	40
0.767	342	41

<sup>1)</sup> Thèses P. 108—109.<sup>2)</sup> Calculated by HENRI i.e. p. 103.

## III.

0.035 N. Salicin solution  $\varepsilon = 0.6$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^4$
0.182	28	13
0.564	121	15
0.685	208	13
0.818	275	16
0.879	341	17

Experiments by V. HENRI on October 10, 1902.

## I.

0.14 N. Salicin solution  $\varepsilon = 0.8$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^3$
0.179	60	31
0.371	177	27
0.505	294	28
0.550	355	27
0.579	415	25

## II.

0.105 N. Salicin solution  $\varepsilon = 0.8$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^3$
0.216	61	39
0.462	176	37
0.606	293	40
0.636	357	36

## III.

0.075 N. Salicin solution + 0.035 N.  
(Saligenin + glucose)  $\varepsilon = 0.8$ .

$\frac{x}{a}$	$t$	$[1-\varepsilon)k_1] 10^5$
0.157	57	28
0.400	172	32
0.539	291	31
0.597	355	32

## IV.

0.105 N. Salicin solution + 0.035 N.  
(Saligenin + glucose)  $\varepsilon = 0.8$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^5$
0.128	59	22
0.344	176	25
0.59	293	23
0.525	357	24

## V.

0.07 N. Salicin solution + 0.97 N.  
(Saligenin + glucose  $\varepsilon = 0.8$ .)

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^5$
0.146	57	25
0.327	173	23
0.376	292	[17]
0.536	355	25

## VI.

0.7 N. Salicin solution  $\varepsilon = 0.8$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^5$
0.221	58	41
0.524	172	50
0.688	291	55
0.712 <sup>1)</sup>	355	49

## VII.

0.035 N. Salicin solution + 0.035 N.  
(Saligenin + glucose)  $\varepsilon = 0.8$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^5$
0.194	57	36
0.469	170	42
0.618	289	42

## VIII.

0.035 N. Salicin solution  $\varepsilon = 0.8$ .

$\frac{x}{a}$	$t$	$[(1-\varepsilon)k_1] 10^5$
0.394	56	95
0.695	170	92
0.880	288	[136]

Experiment communicated by TAMMANN.  
Zeitschr. für physikalische Chemie. 18. 436.

3.007 gram Salicin in 180 cc. water  $\varepsilon = 0.6$ .

$\frac{x}{a}$	$t^2$	$[(1-\varepsilon)k_1] 10^3$	$\varepsilon \times 10^3$ 2)
0.43	1	24	61
0.32	3	25	57
0.58	5	[38]	[75]
0.65	8	30	58
0.76	12	29	52
0.91	26	27	40
0.98	59	28	35

By way of comparison I cite an experiment with amygdalin which I have made in the course of another investigation.

1) In the original paper it says 0.612, but this is probably a mistake.

2) In hours.

3) Calculated by TAMMANN.

The hydrocyanic acid was titrated by LIEBIG's method; in the first period of the reaction, values are found corresponding with those of the sugar determination <sup>1)</sup>).

0.1 N. Amygdalin solution.		
$x$	$t$	$[1-x] k_1] 10^4$
0.507	60	25
0.619	80	26
0.732	120	27

4. These tables show that the immutability of the expression in the third column is satisfactory. In HENRI's experiments those values differ but little more than those of the invertin action. To some extent the experimental errors may certainly be attributed to the sensitiveness of the emulsin and partly also to the method followed. The table with TAMMANN's experiments proves this. The constants vary within rather large limits but agree reasonably with an average value.

5. If we now accept the hypothesis of the negative <sup>2)</sup> autocatalysis, and after what has been stated this seems to me quite permissible, there will be found to exist an evident parallelism between the action of emulsin <sup>3)</sup> and invertin.

The ferment-reactions which up to the present have been accurately studied proceed therefore according to the scheme:

$$\frac{dx}{dt} = (k_1 \pm k_2 x) (a-x) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which  $k_2$  may also be zero <sup>4)</sup>).

This, however, only means that  $k$  is constant for the same series of experiments or for a definite concentration of material <sup>5)</sup> and enzyme.

We may say that there exists a function of the form:

$$k_1 = F(a, b) \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

in which  $a$  is the concentration of the invertible matter and  $b$  that of the ferment.

1) Compare TAMMANN, Zeitschr. für physikalische Chemie, **3**, 27 (1889).

2) This may be one of the causes that the synthetical experiments with emulsin (TAMMANN, EMMERLING) have given a negative result

3) This is probably also the case with other ferment-reactions.

4) It is not inconceivable that cases may occur where if  $t$  is small,  $x$  would at first act positively and afterwards negatively.

5) Up to the present it is only haemase for which SEXTER (Zeitschr. für physikalische Chemie **44**, p. 257, (1903)), has obtained different results within a small concentration limit.

In any case we may conclude that the differential equation (11) is incomplete and that it would be better to give it the form for a reaction of a higher order<sup>1)</sup>.

$$\frac{dx}{dt} = (k_1 \pm k_2 x) (a-x) b \dots \dots \dots (13)$$

which corresponds within certain limits with experience<sup>2)</sup>.

Generally this relation is expressed by the equation:

$$\left(\frac{b_1}{b_2}\right)^n = \frac{k_1}{k_2} \dots \dots \dots (14)$$

From TAMMANN'S<sup>2)</sup> experiments with emulsin it appears that in any case

$$n = P(a, b) \dots \dots \dots (15)$$

It is also important to observe that  $k_1$  is apparently only changeable within the limits of the experimental errors, whether we start from the concentration  $a_1$  of the substances to be inverted or whether we choose as the starting point the concentration  $a_2 + x$ , in which  $a_2 < a_1$  and  $x$  corresponds with an amount of inverted product corresponding with  $a_1 - a_2$ ; HENRI has already pointed this out for invertin.

From  $\frac{ak_2}{k_1} = \text{constant}$  we obtain the somewhat unexpected result:

$$\frac{a}{a} = \frac{k_1}{\gamma_1} = \frac{k_2}{\gamma_2}$$

in which  $a$  and  $a$  represent the concentrations of the substances undergoing inversion,  $k_1$  and  $k_2$ ,  $\gamma_1$  and  $\gamma_2$  the corresponding velocity constants. I hope shortly to revert to this matter.

The matter communicated here has no connection with the later formulation of HENRI<sup>4)</sup> which I cannot yet accept as conclusive.

*Utrecht, Lab. gen. and inorg. Chemistry University.*

1) The formula  $\frac{dx}{dt} = (k_1 - k_2 x) (a - x) = k_2 \left(\frac{k_1}{k_2} - x\right) (a - x)$  represents indeed an expression for a bimolecular reaction.

2) Compare, *Zeitschr. für physiologische Chemie.* **37**, 159. (1902).

There is an evident connection with HORTSEMA'S experiments (*Zeitschr. für physikalische Chemie*) **17**, 1 (1895) but it seems to me that we must not think with HÖBER (*Physikalische Chemie der Zellen und Gewebe*, 1902 p. 312), of any dissociation of the ferment, but rather of that of the substances dissolved therein. Like HÖBER however, I attach no particular importance to an explanation of this kind based on analogy.

3) *Zeitschr. für physikalische Chemie.* **18**, 426, (1895).

4) *Lois générales.* p. 107.

**Geology.** — “*Deep boulder-clay beds of a latter glacial period in North-Holland*”. By Prof. EUG. DUBOIS.

(Communicated by Prof. MARTIN in the meeting of May 30, 1903).

In the dunes near Castricum, borings have been done lately, a provincial lunatic asylum being planned on the spot. With the kind permission of Mr. J. SCHOLTEX, chief-engineer of the “*Provinciale Waterstaat*” in North-Holland, I was allowed to make some hydrological observations and to inspect the specimens of the sediments met with in the borings.

When examining them a remarkable peculiarity came to light, which I subsequently learned to have been found also in a former boring at Uitgeest.

While, namely, in the dunes at Castricum, down to the lowest depth of the borings, no geological facts were observed not known to me from elsewhere, in two boring-holes, at a distance of about half a kilometer from each other, from north to south, at a depth of 32.5 ÷ A. P., a very tough clay was found which possesses all the qualities of boulder-clay. Immediately on it rests a bed, about 12 M. thick, of coarse-grained sand and gravel, which, near to its basis, together with Rhinish pebbles, contains also Scandinavian ones. Very probable — several circumstances point in that direction — many, at least of the latter, had been imbedded in the clay.

As already said, the clay was very tough, mixed however with very angular, finer and coarser grit. Washed, it proves to consist for a large proportion of real clay (hydrous aluminous silicate). Dried it is hard as bricks. In short it is a real, glacial boulder-clay. The colour is bluish-grey; yellow or reddish clay could indeed not be expected at such a depth.

The pebbles from the gravel-bed, and partly no doubt from the clay, are remarkable for their petrographical character.

Besides quartzite of different colours and fine-grained sandstone largely intermixed with mica, white quartz, lydite, flint, there are granite and some other stones of eruptive rock species; amongst others also alnöite, altogether 30 pebbles, all of them evidently of Scandinavian origin, but I also picked up from the gravel, overlying the clay-bed, (part of it apparently had got washed out from the clay-bed by the boring process) some thirty pebbles of Silurian limestone, mostly beyrichian-limestone, of the same kind as those,

well known to me, from the bottom-moraine of the Mirdum Klif in Gaasterland, which fact places their origin beyond any doubt.

The biggest of those limestone pebbles, consisting of coral-limestone, is of 32, the smallest of 8 mM., maximal dimension. A dark slate stone of 33 mM. greatest dimension, shows a polished surface as by ice-action.

The fact that we meet here with a formation of the same kind as the one found on the south coast of Friesland, grew perfectly clear when examining specimens of deposits from borings, done by Mr. A. J. STOEL, near the station of Uitgeest, at 5 or 6 K. M. south-east of those near Castricum. Mr. STOEL, who made also the borings in the dunes near Castricum, had not only kept the specimens of those at Uitgeest, but of many others done by him, which specimens he allowed me to study.

Also at Uitgeest, at a depth equal to that at Castricum, i.e. from 31 M. down to 38 M.  $\pm$  A.P., a large number of stones have been found imbedded in clay, mixed with grit of rocks, perfectly similar in their petrographical character to those at Castricum; those stones were even of considerable dimensions and for more than the half undoubtedly of Scandinavian origin. Under the clay again gravelly sand, to a depth of 43 M., where it rests on a bed of rather stiff clay.

According to communications from Mr. STOEL, the stones, for the greater part, come from the clay-bed, 7 M. thick.

Indeed some of the stones show some still adhering clay. Amongst the rocks are prominent, besides quartzite — of which the biggest stone is 85 m.M., maximal dimension —, white quartz, an odd lydite and sandstone, some pieces of crystalline arkose, from the Bunter on the Rhine, of the size of a walnut, further different eruptive rocks of Scandinavian origin, namely granite, compact porphyry, lestarite, ornöite, especially flint nodules, some of these being 60 mM. But also here, the Silurian limestone-pebbles are the most important; 5 of them have been kept, consisting mostly of beyrichian-limestone, strikingly resembling those which occur in the boulder-clay of the Mirdum Klif.

Those pebbles are of the following dimensions.

- |                                   |                                    |
|-----------------------------------|------------------------------------|
| I. 39 $\times$ 33 $\times$ 24 mM. | II. 44 $\times$ 35 $\times$ 18 mM. |
| III. 33 $\times$ 25 $\times$ 25 „ | IV. 34 $\times$ 33 $\times$ 17 „   |
| V. 30 $\times$ 27 $\times$ 20 „   |                                    |

I and II show unmistakable signs of having been polished and characteristically striated by glacial action, whereas the three others, although not very hard stones, have at least the angular appearance of glacial pebbles.

We may further mention that here, as in the till of the Mirdum Klif, flints and Silurian lime-stones, occur most frequently.

Lately Mr. STOEL gave me a number of Scandinavian stones from a boring at Koog near Zaandam. Amongst these, met with at about 40 M.  $\div$  A.P., are an aln ite of 120 m.M. largest dimension, a granite, not much smaller, different Silurian limestones, one of which is 65 m.M.

The facts stated prove, that in the mentioned part of North-Holland, beneath 31  $\div$  A.P. there is a bed of boulder-clay, a real bottom-moraine. On it rests at Uitgeest and at Castricum, coarse-grained sand and gravel from the lowest part of which, no doubt, some of the described erratica come and which contains shells, marking it to belong to the so called Eem-bed, the equivalent of the *Flandrien* of Rutot.

Of importance, for the comparison of the geological structure with other localities in our North-Sea provinces, is the fact that boulder-clay was lacking at a corresponding depth in two other borings, [about mid-way between the two described] in the dunes at Castricum, one of which went as deep as 45 M.  $\div$  A.P. There, at 40 M.  $\div$  A.P., was a thin layer of 0.30 to 0.40 M., and between 30 to 35 M.  $\div$  A.P. coarse-grained sand and gravel, containing similar small pebbles of beyrichian-limestone. On account of the absence, in the two last mentioned borings, of distinctly marked boulder-clay, the existence of a bottom-moraine, immediately under the Eem-bed, would have been presumed as little here as in most other cases elsewhere. Still proofs of its existence; also in other spots in and near the dunes of the North-Holland mainland are not wanting.

For instance, at borings done, some years ago, in behalf of the Harlem waterworks, at 3 K.M. west of Santpoort and 12.5 K.M. South-west of the boring-hole at Uitgeest, at a depth from 38.75 to 43.75  $\div$  A.P., a bank of sandy clay or rather till was found, 5 M. thick, towards its base changing into sand mixed with clay, which now appeared being only another part of the same bottom-moraine as the one at Castricum and at Uitgeest. Shells of the Eem-bed occur in it, down to 35  $\div$  A.P., although the clay or the till seems to be rather pure, washing shows it for quite  $\frac{1}{4}$  to consist of angular grains of sand, containing some small stones of a peculiar nature. From about 100 cM<sup>3</sup>. of that clay 9 angular pebbles, of beyrichian-limestone were obtained, of which the biggest is 10 m.M., and 12 fragments of eruptive rocks of different kinds, of

which two are of felsite-porphry. An about equal quantity of sharp sand, mixed with clay, taken at the basis, 43.55 M.  $\div$  A. P. deep, produced ten pebbles of the same Scandinavian limestone species, the biggest having 12 mM. maximal dimension, besides 15 pieces of various eruptive rocks, amongst which two of compact porphry. For the rest the specimens contain only a few red and grey quartzites and an odd flint-nodule; the typical Rhinish rocks are at any rate by far in the minority. No doubt this clay of the northern extremity of the prise d'eau of the Harlem waterworks is a boulder-clay of Scandinavian origin, the bottom-moraine of an ice-sheet preceding the deposition of Eem-bed, which is considered to be the youngest stratum of the Diluvium in our country; so the basis of the mentioned bed with sea-shells, indeed corresponds with the end of the last advance of the northern ice. In a recent, much larger boring, in close proximity of the just mentioned one, the uppermost occurrence of Scandinavian stones, measuring 4 c.M. *ad maximum*, side by side with a large majority of stones of Rhinish origin, is found to be at 32 M.  $\div$  A.P. The boring did not go deep enough to reach the boulder-clay bed; but at 33.5  $\div$  A.P. it met with a thin layer of black loam, containing some remains of freshwater-plants. The basis of the Pleistocene shell-bed clearly is at 32 M.  $\div$  A.P.

At Harlem LORIÉ found that basis at 35.6 M.  $\div$  A.P. and I found it at a similar depth myself, in a number of borings done at Harlem, of which Mr. STOEL had kept the specimens. At Velsen, shells characteristic for the Eem-bed are found down to 36 M.  $\div$  A.P.; at Castricum to 31.5 M., at Uitgeest to 31 M.; at Purmerend to 32 M.; at Alkmaar to 34 M.; (a similar figure is given by LORIÉ), at Vogelenzang (according to LORIÉ) to 36.6 M.; in the dunes between Katwijk and Scheveningen, in borings for the Leyden and the Hague waterworks, the shells were found, down to 28 M.  $\div$  A.P.; and at Monster, in borings for the Delft waterworks, down to at least 30 M.  $\div$  A.P.

A little higher, at about 30 M.  $\div$  A. P. average depth, or a few meters less deep, lies in the western chief part of North- and South-Holland, the upper side of a zone of coarse-grained, often gravelly sand, even of real fine gravel, which often contains bigger or smaller stones. It corresponds with a last increase of the geological transport in the Pleistocene, which was connected with a last period of glaciation. Fourteen years ago, its existence was thought not altogether impossible by Dr. LORIÉ, though, (considering the knowledge we then had of the Dutch soil), he did not venture to draw a

more definite conclusion<sup>1)</sup>; the fact that in the *Flandrien* Scandinavian erratic stones occur, was stated by RUTOR<sup>2)</sup> in 1899.

That here indeed we have before us evidence of a glacial period is proved not only by the above stated facts, but also by the other fact that, in the mentioned zone of coarse-grained sand and gravel, often big stones occur, in the very midst of less coarse material, which stones in some cases are of Scandinavian origin. So in the mentioned deep-borings for the Harlem waterworks, at 36 ÷ A. P., a very big pebble of calcareous sandstone was found of which a fragment 11 cM. long has been preserved, and in other deep-borings near the Harlem water-tower, at 33.5 ÷ A. P., a flint of 12 and a quartzite of 7 cM. largest dimension. At Hillegom, where the gravel on the whole is rather coarse, I saw fragments of a reddish sandstone (from the German Bunter), found there at a depth of 32 M. ÷ A. P., which must have been bigger than a fist, and from Heemstede a violet (Bunter) quartzite stone, of 9 cM., largest dimension, raised from a depth of 25.5 ÷ A. P., among small gravel, with many shells. Mr. D. E. L. VAN DER AREND, showed me from borings, done at Adolfshoeve in the Harlemermeer polder, a number of pebbles, raised among coarse-grained sand and fine gravel, amongst which was a grey quartzite of 10 cM. In borings done in behalf of the Leyden waterworks, in the Katwijk dunes, where, just as at Hillegom, the gravel is coarser-grained than mostly elsewhere, at a corresponding depth, pebbles of the size of a walnut, up to that of an egg, were repeatedly met with. Nearly all these stones are of Rhinish origin, giving evidence of transport by floating ice. Mr. J. LANKELMA of Purmerend, told me, that in the many borings he yearly does, he had generally found in North-Holland, at about 30 M. ÷ A.P., stones, sometimes in such a large number and of such a considerable size, that they considerably hindered the borings: even to such an extent, in the Oostschermer polder (Polder K), on the Blokker road and at 1 K.M. south of the church, that they had to throw up the work, any further progress being rendered impossible by the bore striking on an impenetrable stone-bed, immediately under the shell-bed. At Enkhuizen, Mr. LANKELMA found, at an equal depth polished and scratched Scandinavian stones, which he had frequently come across (according to his opinion: granites). From borings done at Alkmaar, Mr. STOEL gave me a fragment almost as

<sup>1)</sup> Bulletin de la Société belge de Géologie, de Paléontologie et d'Hydrologie. Tome 3, (1889), Mémoires, p. 449.

<sup>2)</sup> Ibid. Tome 4, (1899), Procès-Verbaux, p. 321.

big as a fist, of a smooth, but angular stone, consisting of felsite-porphry, raised from a depth of 46 M. ÷ A. P. <sup>1)</sup>)

Those instances may suffice to show the very frequent occurrence, in North- and South-Holland, of evidence of an increased transporting power, in the latter part of the Pleistocene or Diluvium Period, not only of the water, but also of an other means of transport, i. e. by the ice.

The facts known at present, no longer leave any doubt as to the real existence of a younger "gravel-diluvium", here and there alternating with boulder-clay. This younger formation is less powerful than the older "graveldiluvium", for it rarely considerably exceeds ten meters, but it has an equal right as the already long known older and more powerful one to be considered as partially produced by an advance of the Scandinavian land-ice, partially by an increased and modified transporting power of the Rhine, which river then carried much floating ice.

Before concluding I may be permitted to add a thing observed, a year ago, in the boulder-clay of the Mirdum Klif. Amongst other beautifully scratched, glaciated stones, I collected there four, of which three consist of beyrichian-limestone, which are not less typically faceted as those described from the glacial Permian in the Salt Range of the Punjab, from which circumstance it is evident that there is no necessity to suppose for the Palaeozoic glacial period, circumstances entirely different from those of the Pleistocene Ice Age.

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<sup>1)</sup> Towards the east of the Harlemmermeer polder stones occur at a much higher level. This was frequently stated in borings done on the grounds of the military waterworks near Sloten; amongst more other pebbles, I saw a fragment of greenish grey sand-stone, 14 c.M., largest dimension, which fragment had been raised near the Ringvaart of the Harlemmermeer polder, from a depth not greater than 16,5 M. ÷ A. P. A similar fact is known from Aalsmeer. The undisturbed horizontality of the deep peat-layers in this region (the one, more continuous, having its base at 11 or 13 M. ÷ A. P., the other, fragmentary, at about 18 M. ÷ A. P. and nearly continuous to the north and north west, from Purmerend to Hoorn and Enkhuizen and from Wormerveer, Velsen and Beverwijk to IJmuiden, its base being, indifferently, at 17 to 20 M. ÷ A. P.) shows that we have not before us at Sloten and Aalsmeer, the result of a general sloping of the strata, but only a locally higher situation of the upper part of the Diluvium, the coarse sediments having here been locally upheaped.

**Physiology.** — “*On the fact of sensible skin-areas dying away in a centripetal direction.*” By Dr. G. VAN RIJNBEEK. (Communicated by Prof. C. WINKLER).

(Communicated in the meeting of October 31, 1903.)

The manner in which, in our experiments on dogs,<sup>1)</sup> the isolated root-area of the skin (dermatoma), dies away, if the root to which it corresponds, is killed by compression, gives rise to the supposition that this peculiar series of gradually narrowing and shrinking areas, proceeding from ventral to dorsal part, from the lateral parts towards the centrum, may be caused by very simple reasons. This point was demonstrated in our last communication.

In the case of a root being slowly destroyed, its sensibility in the sensible skin-area dies away first in its most peripheral part, continually diminishing further in a centripetal direction. In order to test this conclusion still in another way, I have chosen the old experiment of compressing the nervus ulnaris in the human body. Having taken the necessary precautions for securing a precise localisation of the trauma, I tried this experiment twice on myself. The results, as far as I can judge, were in perfect accordance with the rule, established in our former essays. They may be described as follows: shortly after the compression has begun (by means of a pencil put into the fossa ulnaris), paraesthesia's are observed, principally in the tops of the fourth and fifth finger, descending slowly from thence to extend over the whole of the ulnar side of the hand, and finally ending in perfect insensibility. If the skin of the ulnaris-area is pricked with a sharp pin in the first period of the paraesthesias, it is experienced beyond any doubt that the pain-sensation is much less acute in the little finger than in the lateral part of the hand. Somewhat later a new symptom may be observed: the sensation is becoming distinctly dissociated. At every renewed pricking, at first only a slight touch is felt, and only a little afterwards a sensation of pain sets in, continuing for a rather long period. This symptom of dissociation too has its beginning in the little finger. After some lapse of time it also reaches the lateral side of the hand, whilst in the little finger it has already undergone a change, the interval between the sensation of touch and that of pain having become longer, and this latter sensation greatly diminished.

1) Prof. C. WINKLER and Dr. G. VAN RIJNBEEK. On function and structure of the trunkdermatoma I, II, III, Royal Acad. of Sciences, Amsterdam 1901-'02 and IV *ibid.* 1903.

At last the sensation of pain is wholly lost, and only that of touch remains, till finally the latter too has disappeared, and first the little finger, afterwards also the external lateral part of the hand have become absolutely insensible.

As I said before, these results appear to me to be in perfect accordance — for the pain-stimuli at least — with the rule we have tried to establish: putting to work nearly equal causes, (i.e. both slowly destroying the conduction in a nervepath) the consequences, as well for the sensible ulnaris-area as for the dermatoma, will be equal too. In both skin-areas the pain-sensibility begins dying away in that part, situated at the greatest distance from the centrum, the most peripheral part therefore, this process continuing slowly in a centripetal direction. As to the dissociation, our experiments on dogs have taught us likewise that it may not so very rarely be observed, how the reaction on the pain-sensation, when pinching the sensible area, is retarded. Principally in cases where this area was a small one, or only the remnant of the central area after a very considerable reduction of it. In such cases moreover the pain-reaction was generally very protracted. The results of the experiments taken on dogs and of those tried on myself, are therefore in perfect accordance with one another.

As to the sensation of touch, the experiments on dogs could not teach us anything about this, because it was impossible to make use of any other but pain-sensations for our definitions. The ulnaris-experiment however has shown us, that paralysis of the sense of touch does begin in a later stadium than that of the pain-sensation; whilst its dying away in a centripetal direction cannot be demonstrated with the same evidence as for this latter sensation.

At any rate the first fact is very significant, the more so, if considered in connexion with SHERRINGTON'S communication<sup>1)</sup> on dissociative anaesthesia, as has been explained more fully in our fourth communication<sup>2)</sup> on function and structure of the trunk-dermatoma.

**Physiology.** — *“Structure and function of the trunk-dermatoma”* IV.

By Prof. C. WINKLER and Dr. G. VAN RIJNBEEK.

(Communicated in the meeting of October 31, 1903).

In the course of three preceding communications<sup>3)</sup>, a few observations concerning the structure and the functions of the trunkdermatomata, have been treated of.

<sup>1)</sup> Journal of Physiology. Vol. 27. 1901—02.

<sup>2)</sup> Royal Acad. of Sciences, Amsterdam, Oct. 31, 1903.

<sup>3)</sup> See: Proc. of the Royal Academy Nov. 30<sup>th</sup>, Dec 28<sup>th</sup> 1901, Febr. 22<sup>th</sup> 1902.

At present, guided by some new experiments in this matter, we intend to make an endeavour towards constructing our former results provisorily into a whole, in order to bring the facts, found by means of physiological researches, into accordance with the anatomical records of the peripheral skin-innervation of the trunk.

We know but little with certainty about the topography and the exact form of the different trunkdermatomata in man. Our knowledge of both, such as it is, is due for the greater part to a more just evaluation of the skin-innervation of the *nervi intercostales*<sup>1)</sup>.

It is evident however, that in the physiological experiment the anatomical proportions will have to find their expression on the periphery, and to all probability our dermatomata, determined by physiologic methods, will be proved to be wholly identical with the extension-areas of the skinbranches of the *nervi intercostales*.

According to our belief, on dogs this supposition has been even proved already by our experiments. For by means of a careful examination of a series of central areas, it has been made clear that the differences in shape, manifesting themselves by shortenings or interruptions, may all be retraced to anatomical proportions.

The division of the interrupted central area into a dorsal and a ventral part, follows almost directly from the anatomy of the intercostal nerve, whose skinbranches consist in a posterior and an anterior, respectively a dorsal and a latero-ventral branch. The place where the central area generally suffers interruption, or where in favorable cases on the contrary it is found to be broadest (the lateral part therefore of our trunk-dermatoma) corresponds to the skin-area of the *rami cutanei laterales* of this nerve.

In this way, for the physiologist too, the central area is divided into three individually different parts, form and function of each of which ought to be treated separately. For a knowledge of both is necessary in order to understand the significance of the dermatomata on the extremities.

The dorsal part of the central area is shaped like a truncated triangle, whose basis is situated against the mid-dorsal line. Its apex approaches the lateral line. Between the latter and the mid-dorsal line a line may be traced from the dorsal border of the axilla to the fossa inguinalis.

It has become evident already from our former communications that in favorable cases the dorsal central area towards the mid-dorsal line possesses almost the same breadth as the whole dermatoma.

<sup>1)</sup> BOLK. Een en ander over segmentaal-anatomie etc. N. T. v. Geneeskunde 1897, Vol. II, N<sup>o</sup>. 10.

In less favorable cases it is narrowed, in very unfavorable ones it has shrunk away to the sensible area situated at a small distance from the mid-dorsal line (fig. 1, 2, 3, 4, *a*). It is there (see fig. 1 *a*) that is situated a maximum of the dorsal part of the central area, at the same time the ultimum moriens of the whole dermatoma.

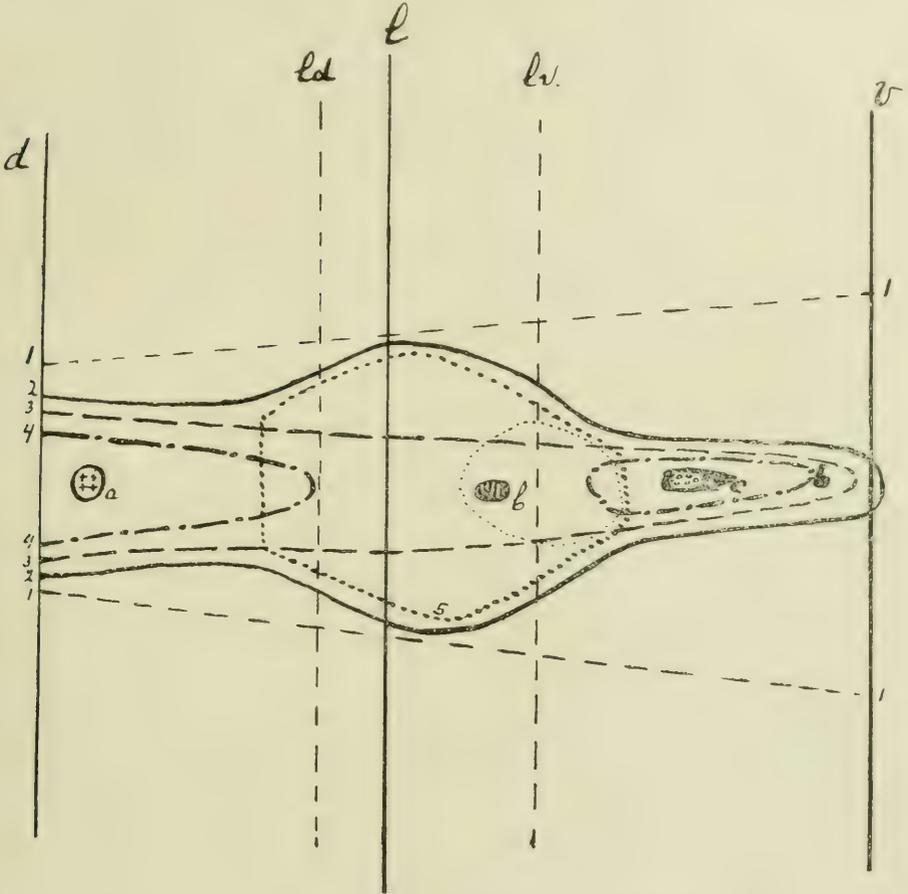


Fig. 1. The different parts of the dermatoma.

*d* = mid-dorsal line.

*v* = mid-ventral line.

*l* = lateral line.

*ld* = dorso-lateral limitline (from dorsal border of axilla to fossa inguinalis).

*lv* = ventro-lateral limitline (from ventral border of axilla to fossa inguinalis).

1 = Boundaries of the theoretical dermatoma.

2 = Boundaries of the dermatoma (central area) as it may be observed in very favorable cases.

3 = Boundaries of the central area in less favorable cases.

4 = Boundaries of the dorsal part of the central area and 6 = Boundaries of the ventral part of the central area as they are observed in very unfavorable cases with interrupted central areas.

5 = Boundaries of the lateral part of the central area.

 *a* = dorsal,

 *b* = lateral,

 *c* = ventral maximum.

The lateral part of the central area, more difficult to be rendered because of its great variability of form, may be represented, in cases very favorable to isolation, by a nearly hexagonal figure (see fig. 1, 5). In very unfavorable cases it cannot be shown at all. In such cases the central area appears to be interrupted. Between both extremes other cases may be observed, in which the lateral central area has been only partly preserved.

An instance may be forwarded by the following observation:

1. On a strong male dog the 16<sup>th</sup> dermatoma is isolated in the usual manner. The day after the operation a central area is determined, the extension of which is represented in fig. 2. Possessing a broad basis at the mid-dorsal line, it ends in a point towards the mid-ventral line.

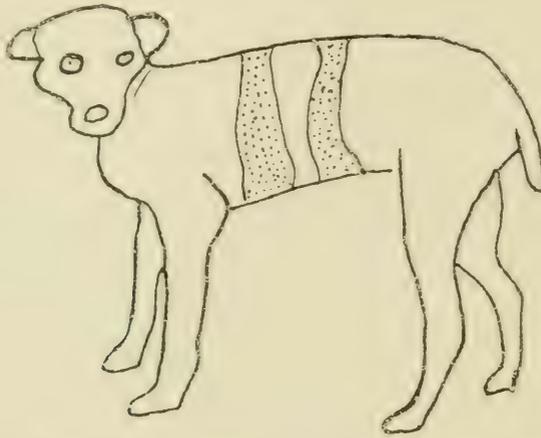


Fig. 2. A continuous central area, extending itself from the m. d. l. to the m. v. l.

After two days, this area has fallen asunder into three parts, viz. a triangular area towards the mid-dorsal line, a rhomboidal area towards the mid-ventral line (see fig. 7), and a circular area situated between the former two (see fig. 3).

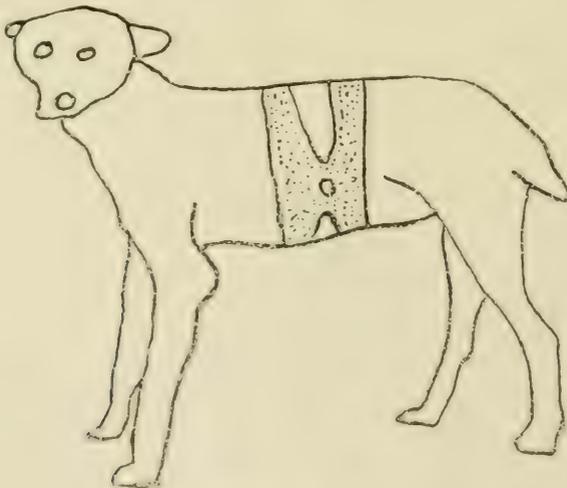


Fig. 3. After two days, this area has fallen asunder into three parts.

Evidently in this case the three separate parts, into which the originally continuous central area of the dermatoma has divided itself as it were under our very eyes, may be considered as the *three* unities which we believed ourselves justified in distinguishing in the dermatoma <sup>1)</sup>, their considerable shrinking having made it possible to demonstrate each of them individually.

For these same reasons the small circular area between the dorsal and ventral parts, signifies here a maximum (see fig. 1 *b*) in the lateral part of the central area, similar to the one shown already in the dorsal part.

Though it may not be found very often, the foregoing observation stands in no wise alone. In the experiment also, from which the annexed fig. 4 was taken, the central area, having fallen asunder into three pieces, might be observed for more than a week.

The proportional rarity of this last maximum may be easily accounted for. In the first place it is relatively a feeble maximum. If therefore the traumatic lesion of the central area is too important, the maximum is destroyed, together with the whole lateral part. If on the contrary it is not important enough, in such a manner that, although there has been an interruption of the central area, still a larger part of the lateral piece remains unimpaired, the sensible remnant of the lateral piece will confound itself with the ventral piece. In order therefore to demonstrate an isolated maximum, we need a certain degree of exhaustion of the lateral piece, not strictly definable, not strong enough to render this part quite insensible, yet sufficiently strong to destroy its eventual connexion with the ventral piece. <sup>2)</sup>

Finally the ventral part of the central area. This may be represented as an oblongly stretched oval along the mid-ventral line (see fig. 1, 6.).

Very rarely this may be observed as an isolated whole, because it easily unites itself with a part of the lateral piece of the central area, situated roundabout the lateral maximum. Still the case does present itself sometimes, whether or no the maximum of the lateral part has been preserved. Fig. 5 and 6 offer instances of this case, whilst in fig. 7 the same dog, represented already by fig. 2 and fig. 3, is designed in another attitude, in order to show the ventral part.

<sup>1)</sup> See the Proc. of the Royal Acad. of Sciences, mentioned before.

<sup>2)</sup> See: Proc. of the Royal Acad. Nov. 30<sup>th</sup> 1901, fig. 4 and also: G. WINKLER. Ueber die Rumpfermatome. Monatschrift für Psychiatrie und Neurologie. Bd. XIII. Heft 3.

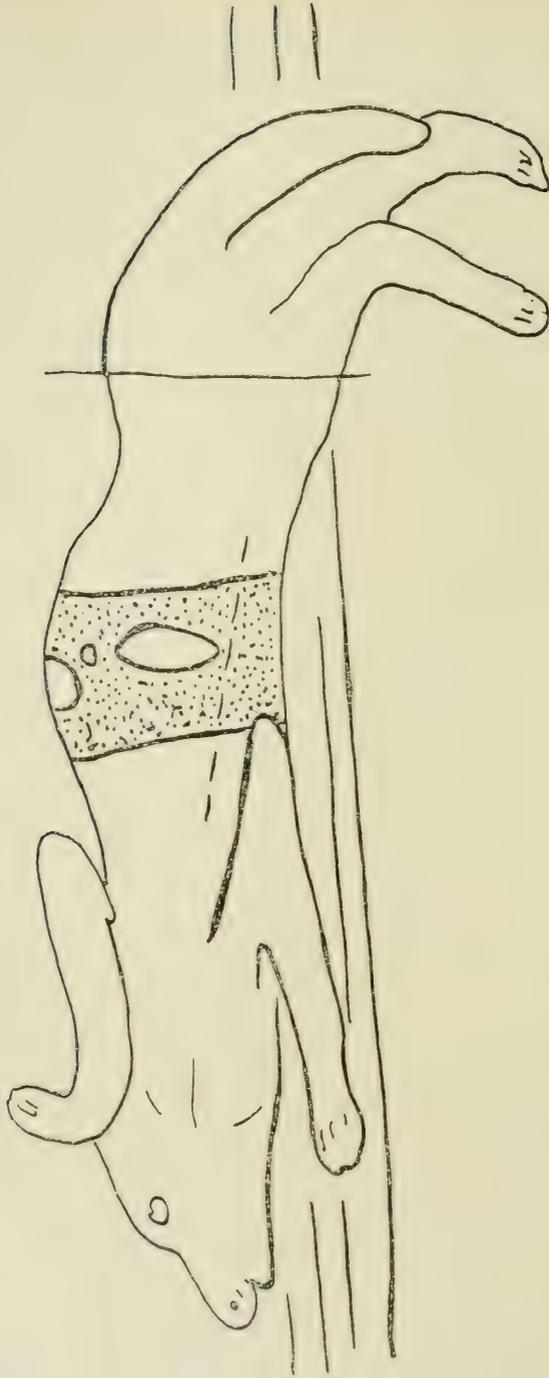


Fig. 4. Another dog, showing the three parts of the central area.

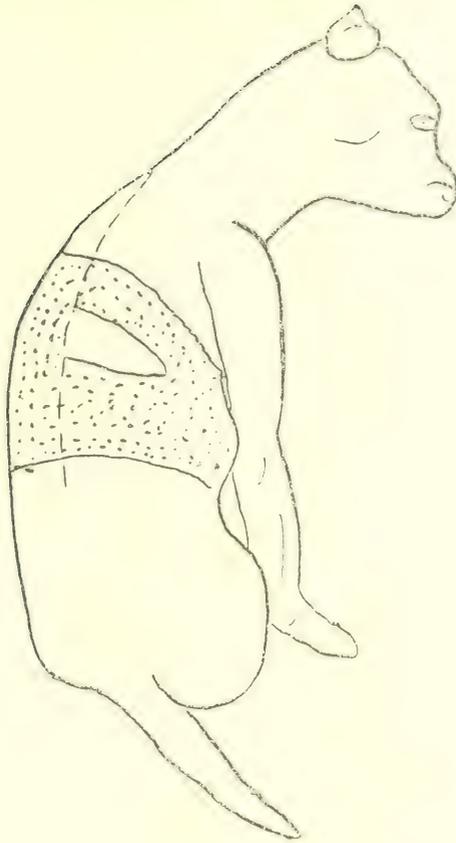


Fig. 5.

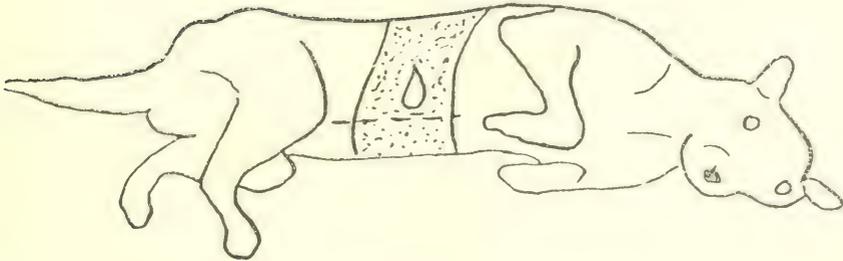


Fig. 6.

Fig. 5 and 6. Dorsal and ventral central area, defined two days after the operation.

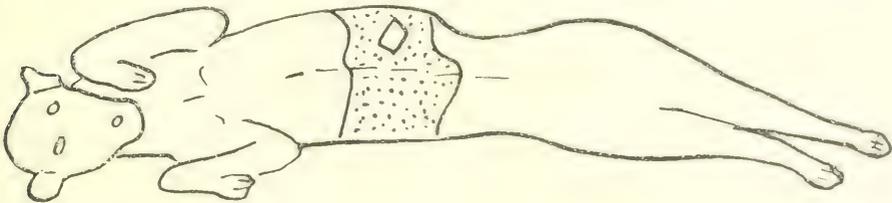


Fig. 7. The same dog from Fig. 2 and 3, photographed in another attitude in order to show the whole of the ventral piece of the central area.

The ventral part of the central area too possesses its maximum, still to be demonstrated in cases, where the maximum of the lateral central area (see fig. 6) has already descended under the threshold of sensibility, and is therefore lost.

It is of a somewhat rhomboidal form (see fig. 1 *c*).

In resuming the total of our observations, we obtain for the trunkdermatomata the following results:

1<sup>st</sup>. The central area is composed of three parts of distinct significance, their individual difference showing itself already in the manner in which they overlap one another. <sup>1)</sup>

2<sup>nd</sup>. They may be demonstrated independently of one another.

3<sup>rd</sup>. Each of them suffers in a different way the reducing influence of the operative trauma.

4<sup>th</sup>. Each of them individually possesses a maximum, centre or ultimum moriens: in this manner that the ultimum moriens of the dorsal piece must be understood at the same time to be that of the whole dermatoma.

5<sup>th</sup>. Each of them corresponds to the extension-area of a different branch of the intercostal nerve.

Starting from these facts, an endeavour may be made to explain the singular reduction of the sensible area, because of which it becomes only possible to demonstrate that part of the dermatoma we have called its central area. Though its cause certainly ought to be sought in the operative trauma, yet this accounts in no wise for the different manner, in which the reduction may be observed in the dorsal, lateral and ventral parts of this central area.

The pointed narrowing of the central area towards the ventral side, hitherto has been accounted for by the greater stretching of the ventral part of the trunkskin as compared with its dorsal part. It was supposed that an originally equal number of nerve-arborisations existed on the dorsal as on the ventral side. This number being extended over a larger surface — as is the case for the ventral side — the result will be a higher threshold of sensibility on this side. In our nomenclature this was called: enlarging of the marginal area at the expense of the central area.

Partly too, the perhaps still larger extension, caused by the growth of the extremities, may be called in aid to explain the fact, that the lateral piece is at once the broadest as well as the feeblest part of the dermatoma. But yet there must needs be found another collaborating factor, if we intend clearing the apparent contradic-

<sup>1)</sup> See: Proc. of the Royal Acad. Febr. 12<sup>th</sup> 1902.

tion, that it has been proved impossible to isolate a ventral piece, the breadth of which is in any way comparable to that of the dorsal, much less to that of the lateral part. For though the stretching of the lateral piece caused by the growth of the cone of the extremities, must be very considerable, yet it does not become sufficiently clear at first sight why it should be precisely the ventral parts of the dermatomata that remain the narrowest portions of the central area, even in the most favorable cases.

We believe it is in the peripheral relations of the skin-innervation, that the factor will be found, accounting for the fact that, *in favorable cases*, the lateral part of the dermatomata has been observed to be so much broader than the ventral part.

Experience has taught us that *each single part of the central area is slowly becoming insensible from its periphery towards its maximum or centrum, and that the central area as a whole does the same from ventral towards dorsal side*, and as these maxima or centra correspond with tolerable accuracy to the entrance-place of the peripheral sensible nerves, some explanation is already afforded.

The maxima thence would be those places situated nearest to the centrum (ganglion or medulla). If now by means of a trauma hitting the nerve-root, the free conduction of stimuli is hindered, the stimuli, retaining their activity longest, will be those that are enabled to reach the centrum along the shortest path from the root-region. This rule prevails for the whole dermatoma as well as for each single part of the central area. In the case of dogs, where the medulla is situated very close to the back, the distance from ventral skin to medulla is at least twice as large as the distance from back to medulla. For this reason alone already, the ventral part, independently of its greater extension, will be the first to be reduced, and the ultimum moriens of the whole dermatoma will be found opposite the entrance-place of the dorsal skin-branch into the dorsal piece of the central area. The lateral piece of the central area, being put by its tension into unfavorable conditions, probably even more unfavorable than those of the ventral piece, still remains less ill-conditioned than the ventral piece of the central area, because of the shorter path followed by the stimuli in order to reach the medulla. In cases favorable to isolation, it is to this latter factor that we have to look for discovering the final cause, why the lateral piece remains very broad, and why the ventral piece, its nerve-path being so much longer, becomes narrowed. In cases unfavorable to isolation on the contrary, it is the other factor that prevails, and

the greater tension causes the lateral part to become insensible earlier than the ventral part.

This opinion is supported by the facts which we may observe, when compressing a peripheral nerve, e. g. the *nervus ulnaris*. In that case too, the sensibility for pain-stimuli slowly dies away from the periphery of the innervation-area on the skin towards its centrum, i. e. the entrance place of this nerve into the innervation-area.

The recent communications of SHERRINGTON<sup>3)</sup> too, apparently point to this same fact: the central areas dying away slowly in a centripetal direction.

His third conclusion especially may be said to be of importance in this matter: "In the skin of macacus the "pain-field" and the "heat-field" of a single sensory spinal root, at least in the case of certain spinal nerves, are each less extensive than is the "touch-field" of the same root."

As in our experiments the stimuli employed were exclusively maximum pain-stimuli, a doubt may arise, whether our central-areas ought not to be considered simply as those areas of the dermatoma that are sensible to pain. The peculiar way, in which the intensity of the operative trauma exerts its influence on the form of the central area, renders this supposition highly improbable. Much more probable it is, that the before-mentioned conclusion of SHERRINGTON expresses in a different manner that the pain-sensibility in sensible skin-areas is dying away in a centripetal direction. The sensibility for pain however — and the *ulnaris*-experiment also points this way — is lost much sooner than the sense of touch. Experiments made by one of us on sharks, that will be communicated afterwards, are in accordance with this observation.

Both the peculiar proportions of the peripheral skin-innervation (entrance-places, extension-areas of the skin-branches in the root-area), and the general rules for the nerve-conduction, are therefore of equal importance for determining experimentally the form of the dermatomata.

Because three afferent nerves of different significance innerve three pieces of the trunkdermatoma, possessing each of them a different degree of extension, the sensibility for pain, decreasing (in cases of progressive lesions) in a centripetal direction, will be the cause of the apparently capriciously-shaped central areas, described in the course of our observations.

<sup>3)</sup> SHERRINGTON, On dissociative anaesthesia (*Journal of Physiology*, vol. 27, 1901-'02).

**Physics.** — “*On the equilibrium between a solid body and a fluid phase, especially in the neighbourhood of the critical state.*”  
(II part). By Prof. J. D. VAN DER WAALS.

In my former communication the curve of the three-phase-equilibriums was considered as the section of two  $(p, T, x)$  surfaces, viz. that of the two fluid equilibriums, and that of the equilibriums between solid and fluid phases. For anthraquinone and ether this section consists of two separate parts, one on the side of the ether, and the other on the side of the anthraquinone. For values of  $x$  ranging between two definite values, the two mentioned surfaces do not intersect. These values of  $x$  are nearer to each other than those of the critical phases coexisting with the solid body. I have indicated them in my preceding communication as a maximum value or a minimum value of  $x$ . We might also distinguish them by writing  $x_e$  and  $x_a$  for them. Then  $x_e$  is the smallest value of  $x$  for which the two  $(p, T, x)$  surfaces have still a point in common on the side of the ether. In the same way  $x_a$  is the largest value of  $x$  for the corresponding point on the side of the anthraquinone.

In order to examine closer the particularities which take place in the points in which the two  $(p, T, x)$  surfaces separate, it is useful, to draw besides the  $p, x$  sections of the preceding communication, also the sections of the two  $(p, T, x)$  surfaces for constant value of  $x$ . As the particularities in the points, at which the two surfaces separate, differ on the side of the ether from those on the side of the anthraquinone, I have drawn the two following figures, fig. 7 representing the particularities on the ether side, and fig. 8 those on the other side.

In fig. 7 we see first traced the well-known loop for the fluid equilibriums, (Cont. II, p. 138). It is taken for the value of  $x$  of the critical phase on the side of the ether, which coexists with the solid body. Let  $P$  represent that critical phase and so be the plaitpoint. This plaitpoint has been chosen left of the maximum pressure, in accordance with the circumstance that the plaitpoint pressure will most likely increase with the temperature. In this point the two  $(p, T, x)$  surfaces would have a common tangent, which would be normal to the plane of the figure, and so does not appear in the figure given. This common tangent is of course a tangent to the section of the two surfaces, which section is projected on the plane of the figure as the  $(p, T)$  curve for the three-phase-equilibriums. As in this  $(p, T)$  curve the value of  $p$  increases with  $T$ , it may be traced in two ways; either as has been done in the

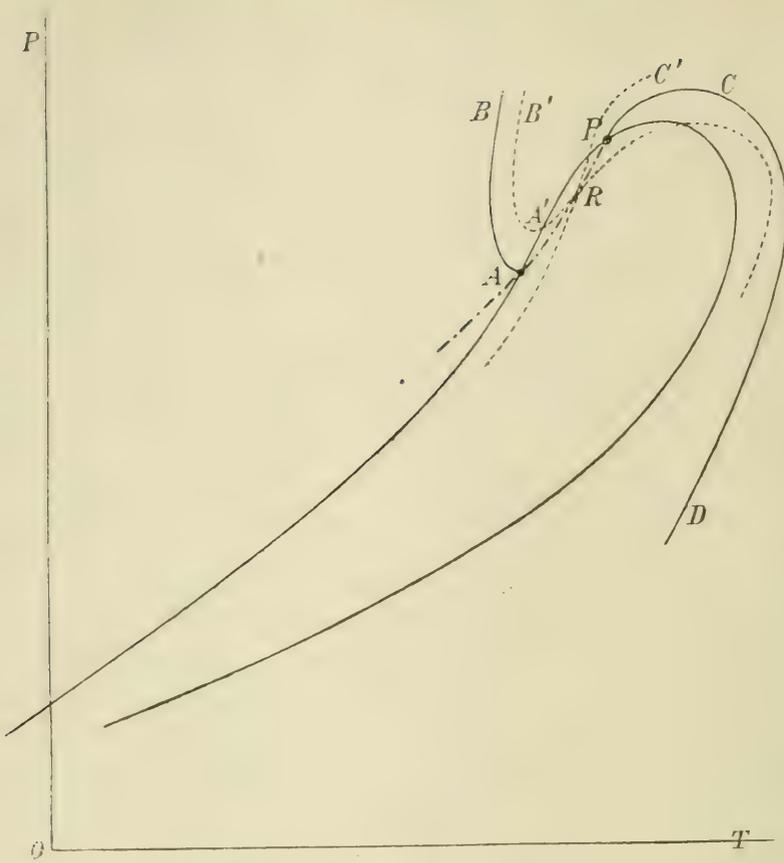


Fig. 7.

figure, passing through a point  $A$  of the upper branch, or through a point which has not been indicated and which would lie on the lower branch. This projection of the three-phase-pressure is denoted by a curve, which consists of alternate dots and dashes. So besides  $P$ , also the point  $A$  is a point of the section of the two  $(p, T, x)$  surfaces for the value of  $x$  chosen; the point  $A$ , however, at lower temperature. The two curves  $AB$  and  $PCD$  indicate further points of the section for constant value of  $x$  of the solidfluid surface, in so far as this section does not lie within the region, in which one fluid phase splits up into two fluid phases (liquid and vapour). Instead of the theoretical course of the section between the point  $A$  and  $P$ , we get the three-phase-pressure.

There is one circumstance, which decides whether the course of the curve of the three-phase-pressure is as it has been traced, so running to a point  $A$  of the liquid sheet, or whether it ought to run to a point of the vapour sheet. For a value of  $x$  lying nearer

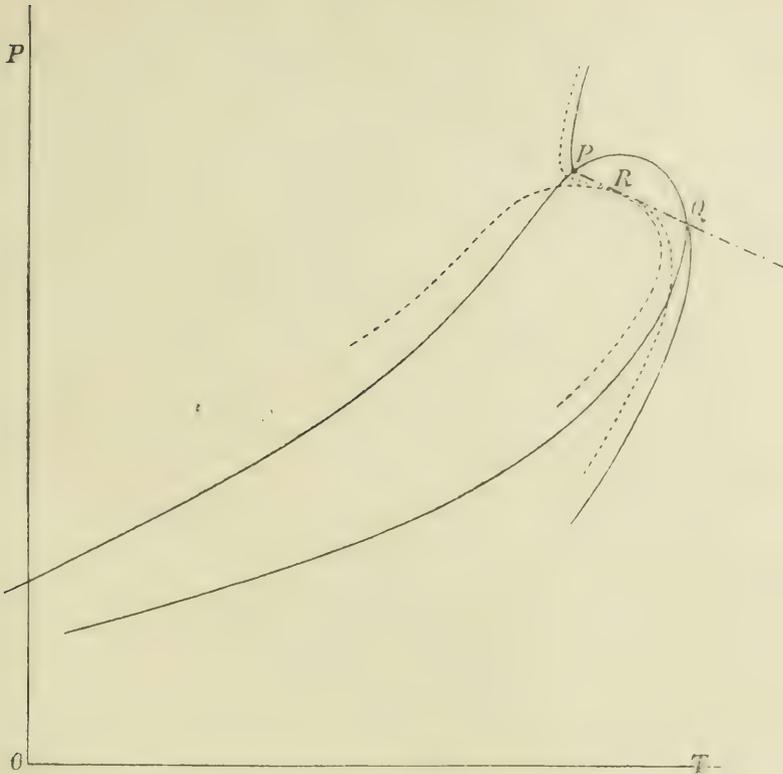


Fig. 8.

to the side of anthraquinone, the theoretical part, in whose stead we get the three-phase-curve, must become *smaller*, and it will finally contract to a point of contact lying somewhere on the curve  $AP$ . If therefore for a certain smaller value of  $x$ , the above mentioned curves are drawn as has been done by the dotted curves, the deformation and displacement of the other curves must be such, that a point of contact can occur on the line  $AP$ . So the question is, to what modification must the  $(p, T)$  curve of the fluid equilibriums be subjected, when it is traced for smaller value of  $x$ . The answer to this question is given by the sign of  $\left(\frac{dp}{dx}\right)_T$ . Both for the equilibriums between two fluid phases and for those between a fluid and a solid phase, this quantity is positive as a rule. Only in a limited region reversal of sign may take place. But this does not prevent us from seeing immediately, that in fig. 7 for smaller values of  $x$  the main position of the liquid-vapour curve will have to be lower — and in order to be able to touch the curve  $AP$  the position of this latter curve must be as it is drawn. If it had the other

position which has been stated as possible, the contact could only be brought about by drawing the dotted lines higher. In the first place this proves that the last point which the two  $(p, T, x)$  surfaces have in common, lies on the upper sheet of the equilibriums between the fluid phases and secondly, that the section of the surface of the equilibriums of the solid phase for the value of  $x$  of the point of contact must have besides two vertical tangents, also two horizontal tangents. This is in so far in concordance with what has been observed on p. 240 of the preceding communication, that a similar course for such a curve has been given there. But in so far different, that on account of an incomplete investigation the opinion was expressed there, that the two horizontal tangents are subjected to the condition  $\frac{\partial^2 \psi}{\partial n^2} = 0$ . For, if they were subjected to this condition, they would exist theoretically, but they could not be realized. I shall continue and complete the investigation of p. 240 presently, when it will appear, that the shape derived in fig. 7 for a section can occur at constant  $x$  and that it can really show a maximum and a minimum in the realizable part.

But let us now proceed to examine fig. 8. There the particularities of the contact of the curves are drawn in the neighbourhood of the  $x$  of the second critical phase which can coexist with the solid body, viz. that which is richer in anthraquinone. Again for the  $x$  of the critical phase the  $(p, T)$  curve has been drawn of the equilibriums between the fluid phases, and the plaitpoint  $P$  on this curve has been chosen left of the maximum pressure. If the course of this plaitpoint curve should be such that  $\frac{dp}{dT}$  is negative for this plaitpoint, we ought to have chosen it right of the maximum pressure. But for our purpose the place where  $P$  is chosen, whether right or left of the maximum pressure, is of no account. Only  $P$  must not be chosen on the lower sheet, as would be the case for *R. C. II*. Also the projection of the three-phase-pressure has been drawn this time, in concordance with the fact, that  $p$  decreases with increasing value of  $T$ . Now that  $P$  is chosen on the left, the three-phase-pressure need not decrease so rapidly, as would be the case, when  $P$  was chosen on the right. The points  $P$  and  $Q$  of this figure are now two points of the section of the two  $(p, T, x)$  surfaces for the value of  $x$ , which we may denote by  $(x_k)_n$ . For the point of contact of the two surfaces we must know the circumstances at  $x_n$ , which value is larger than  $(x_k)_n$ . Now we shall be able to bring about the contact, which is assumed to take place in the figure in point  $R$ , by raising

the curve of the equilibriums between the fluid phases, which is necessarily attended by contraction. In this position the  $(\rho, T)$  curve of the equilibriums between solid and fluid phases need not show the maximum and the minimum of  $\rho$ , and only the necessity of the two vertical tangents remains. For still larger values of  $v$  and so for  $v > v_a$ , the two curves, which are dotted in fig. 8 and touch in  $R$ , and which also touch the curve of the three-phase-equilibriums in the same point, are separated, and the  $(\rho, T)$  curve of the equilibriums between solid and fluid phases surrounds the equilibriums between the fluid phases altogether, so that the latter could only appear in consequence of retardation of the appearance of the solid phase.

What precedes fully explains in a graphical manner the way in which the two  $(\rho, T, v)$  surfaces get detached, and it remains only to complete the discussion of p. 240 on the course of  $\left(\frac{d\rho}{dT}\right)_{x_f}$ , which

has not been fully carried out there. For the determination of this quantity we have the equation:

$$T \left(\frac{d\rho}{dT}\right)_{x_f} = \frac{W_{sf}}{V_{sf}}$$

The course of the denominator in the second member, viz.  $V_{sf}$ , has been discussed p. 233. It has been proved there that a locus exists in the  $(V, v)$  diagram, generally consisting of two branches, outside which this quantity is negative. These two branches are further apart than the points  $D$  and  $D'$  (fig. 2 of the preceding communication), and at least in the neighbourhood of the plaitpoint, also further apart than the points of the spinodal curve and even the connodal curve. It is possible and even probable that the two branches of this locus meet. If namely the direction of the tangent in the inflection point of an isobar points just to the point  $P_s$  of the figure 2, the two branches coincide. And whereas in the point  $K$  the direction of the tangent is parallel to the  $v$ -axis in the inflection point, in inflection points more to the right of the isobars the tangent mentioned assumes more and more a position, directed to  $P_s$ . This locus, for which  $v_{sf} = 0$ , is therefore a curve closed on the right, just as is the case with the connodal curve and the spinodal curve and the curve of the points  $D$ , for which  $\frac{\partial^2 \psi}{\partial v^2} = 0$ . Outside this region  $v_{sf} < 0$ , and inside  $v_{sf} > 0$  — only in that part of the region, however, that lies outside the locus of the

points  $D$ . If however we take the product of  $\frac{\partial^2 \Psi}{\partial v^2}$  and  $v_{sf}$ , we need not make a difference for the points inside  $v_{sf} = 0$ , and we may assume that outside the locus, for which  $v_{sf} = 0$ , this product is negative and inside it, positive. I need hardly mention, that just as the connodal curve, the spinodal curve and the curve  $\frac{\partial^2 \Psi}{\partial v^2} = 0$  are modified and displaced according to the temperature, also the curve  $v_{sf} = 0$  depends on the value of  $T$ . On the whole it will contract and move towards the side of the anthraquinone with increase of temperature, and so follow the same course as the other loci mentioned.

The course of the value of the denominator, viz. of  $W_{sf}$ , has not yet been discussed. In the preceding communication I had thought that I could leave out this discussion, first because I did not think it necessary at all, but also because I thought that the result of this discussion could not be brought under a simple form, and finally, because I did not wish to add another to the number of loci.

The particularity in the course of the  $(\rho, T)$  curve, for the equilibrium between solid and fluid, however, to which we have had to conclude in fig. 7, has proved, that the discussion is not to be evaded, at least if we wish to explain fully by theoretical means, the way in which the two  $(\rho, T, x)$  surfaces get detached. And the result of the discussion of the quantity  $W_{sf}$  has proved to be very simple — and almost exactly the same as the result of the discussion concerning the quantity  $V_{sf}$ . Just as there is a locus for which  $V_{sf} = 0$ , so there is one for which  $W_{sf} = 0$ . Just as the curve for which  $V_{sf} = 0$  consists of two branches further from each other than the points  $D$  and  $D'$  of fig. 2, which two branches meet outside the top of the plait, in the same way the curve  $W_{sf} = 0$  consists of two branches, further from each other than the points  $D$  and  $D'$ , and these two branches meet also, either outside the top of the plait, or inside it. And finally the locus, for which  $W_{sf} = 0$ , lies entirely within that for which  $V_{sf} = 0$ . The resemblance goes further. Outside  $V_{sf} = 0$  this quantity is negative, and outside  $W_{sf} = 0$  the value of  $W_{sf}$  is negative. Inside  $V_{sf} = 0$  the quantity  $V_{sf}$  is positive and increases to infinite when we reach the points  $D$  and  $D'$ , being again negative inside these limits. The same applies to the quantity  $W_{sf}$ . Inside the curve for which  $W_{sf} = 0$ , this quantity is positive. In the curve of the points  $D$  and  $D'$  the value has increased to infinite, being again negative inside the points  $D$  and  $D'$ . If we

examine the product  $\frac{\partial^2 \Psi}{\partial v^2} W_{sf}$ , we see that this product is negative outside  $W_{sf} = 0$ , and positive inside it.

There is therefore only a small region, in which the quantities  $W_{sf}$  and  $V_{sf}$  have different signs, namely that region inclosed between the loci, for which these quantities are zero. In this case  $\left(\frac{dp}{dT}\right)_{x_f}$  is negative. In fig. 7 this is the case for some points on the

curve  $B'A'RC'$  on the left of  $A'$ , so for the points lying between the point for which the tangent is vertical, and the point  $A'$ , for which the tangent is horizontal. In the same way for some points on the right of the maximum, up to the point where the tangent is vertical.

In order to arrive at this result as to the course of the quantity  $W_{sf}$ , I had first brought this quantity under the form which has been given Cont. II, p. 110, for the analogous case of the equilibrium between two fluid phases, viz:

$$W_{sf} = pV_{sf} + \varepsilon_s - \varepsilon_f - (v_s - v_f) \left(\frac{d\varepsilon_f}{dv_f}\right)_{pT}$$

We may write then (I refer to the page cited of Cont. II and the following page for the signification of the notation):

$$T \left(\frac{dp}{dT}\right)_{x_f} - p = \frac{(\varepsilon_{sf})_p}{V_{sf}}$$

If we represent in a figure the value of  $\varepsilon_f$  for a curve of equal pressure, passing through the unstable region, e.g.  $BEDD'E'B'$  of fig. 2, we obtain a curve as is represented in fig. 9. The points of this curve, for which  $\varepsilon_f$  is small, represent the energy of the liquid states corresponding to this pressure. The points lying between the two vertical tangents represent the value of  $\varepsilon_f$  for the unstable phases, and the remaining points represent the energy for what we may call gas states. The absolute height of the curve is not determined by anything, as it represents energy. Only if we also represent the energy of the solid body, the latter energy, being smaller than that of the liquid phase of the same concentration and of the same pressure and temperature, will be indicated by a point lying below the curve traced. I have represented it by  $\varepsilon_{P_s}$ . Whenever the tangent to this curve cuts the axis above  $\varepsilon_{P_s}$ ,  $(\varepsilon_{sf})_p$  is negative and vice versa.

The same circumstances which occur for the sign of  $V_{sf}$ , are also found here.

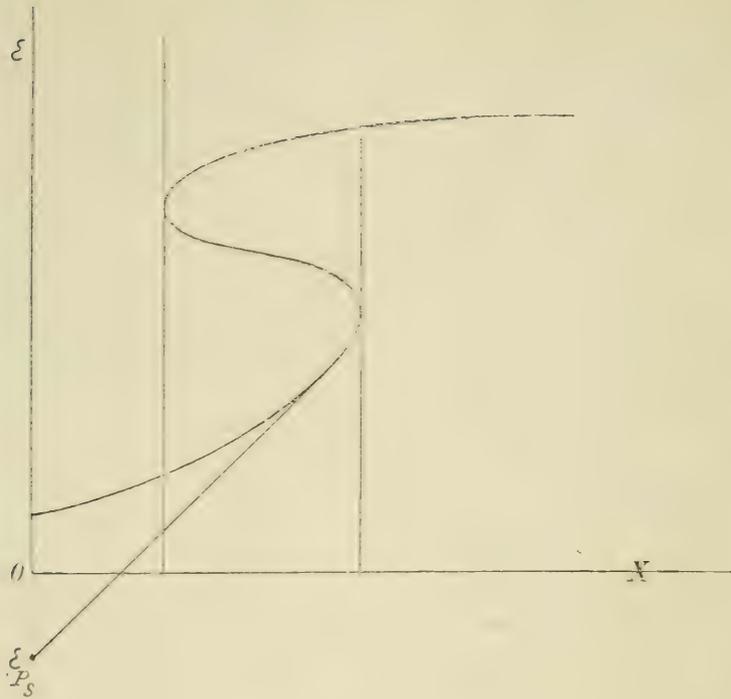


fig. 9.

But though I have concluded to the course of this value of  $W_{sf}$  above mentioned from considerations derived from this figure, I have understood afterwards, that we may acquire a survey of this course in a simpler way. We may give  $W_{sf}$  a somewhat different shape, which occurs on p. 1 Cont. II, viz. :

$$W_{sf} = \left[ \mu + \left( \frac{\partial \epsilon_f}{\partial v} \right)_{T, p} \right] \Gamma_{sf} (\epsilon_{sf}),$$

About the quantity  $(\epsilon_{sf})_v$  we know, that it is negative, save for the exceptional case of water below  $4^\circ$ .<sup>1)</sup> Of  $\Gamma_{sf}$  we know, that inside the locus for which this quantity is equal to zero, it is positive and increases rapidly, till it is infinitely large on the curve of the points  $D$  and  $D'$ . And as the factor of  $\Gamma_{sf}$  is necessarily positive, it follows, that  $W_{sf}$  is equal to zero on a curve, which lies between that for which  $\Gamma_{sf}$  is equal to zero, in which case  $W_{sf} = (\epsilon_{sf})_v$  and negative, and the curve, on which  $W_{sf}$  is positive and has risen to infinitely large. The latter curve is that of the points  $D$  and  $D'$ . We have come to the conclusion that the curve  $\Gamma_{sf} = 0$  in the

<sup>1)</sup> See for the value of  $(\epsilon_{sf})_v$  also "Ternary systems III." These Proc. IV p. 682.

neighbourhood of its tops passes round the top of the plait in a fairly wide circle, so that it also encompasses the plaitpoint. We know about the curve of the points  $D$  and  $D'$ , or the points for which  $\frac{\partial^2 \Phi}{\partial v^2} = 0$ , that its top lies inside the plait. As to the new locus

$\bar{V}_{sf} = 0$ , which lies between them, we do not know a priori how its top is situated with regard to the top of the plait. We may only expect, that when there is a great distance between the tops of the plait and those of the points  $\bar{V}_{sf} = 0$ , there is a greater chance that also the locus  $\bar{V}_{sf} = 0$  will pass round the plait. For the plaitpoint of fig. 7 the latter case has then be realized. For the plaitpoint of fig. 8 probably the opposite case.

For the points, for which  $\bar{V}_{sf} = 0$ , we get :

$$T \left( \frac{dp}{dT} \right)_{x_f} = p + \left( \frac{\partial \epsilon_f}{\partial v_f} \right)_{T, \dots}$$

or

$$\left( \frac{dp}{dT} \right)_{x_f} = \left( \frac{\partial p}{\partial T} \right)_{v, x}$$

We might immediately have come to this conclusion. For from :

$$d\mu = \left( \frac{\partial \mu}{\partial T} \right)_{v, x} dT + \left( \frac{\partial \mu}{\partial v} \right)_{T, x} dv + \left( \frac{\partial \mu}{\partial x} \right)_{T, v} dx$$

follows the above relation, keeping  $x$  constant, and  $\frac{\partial \mu}{\partial v}$  or  $\frac{\partial^2 \Phi}{\partial v^2}$  being zero.

If we write :

$$T \left( \frac{dp}{dT} \right)_{x_f} = T \left( \frac{\partial p}{\partial T} \right)_{v, x} + \frac{(\epsilon_{sf})_v}{\bar{V}_{sf}}$$

and now take into consideration that  $(\epsilon_{sf})_v$  is negative, we derive:

$$\left( \frac{dp}{dT} \right)_{x_f} > \left( \frac{\partial p}{\partial T} \right)_{v, x_f}$$

when  $\bar{V}_{sf}$  is negative and vice versa.

If we compare the value of  $T \frac{dp}{dT}$  for the three-phase-pressure in the immediate neighbourhood of a plaitpoint, with the value of  $T \left( \frac{dp}{dT} \right)_{x_f}$  for the equilibrium of solid and fluid phases in the next point, it may be demonstrated in several ways, that these quantities have the same value. In fig. 7 it has been really represented like this, but in fig. 8 we see in the neighbourhood of  $P$  a sudden break in the direction of the pressure, which does not exist in reality.

The curve extending upwards from  $P$  should therefore be bent in such a way, that its initial direction was the same as that of the curve of the three-phase-pressure.

The tangent plane to the  $(p, T, x_f)$  surface being normal to the plane of the figure, because it contains a line which in  $P$  is normal to the figure, every curve on that surface, passing through  $P$ , will have its projection in the section of the tangent plane with the plane of the figure; and so both the curves extending upwards from  $P$  and those extending downwards, will have their projections in this same section. This follows also from the values of p. 241 (preceding communication). We have for the three-phase-pressure:

$$T \frac{dp}{dT} = \frac{\frac{w_{s_1}}{v_{s_1}} - \frac{w_{21}}{v_{21}}}{x_s - x_1} \cdot \frac{\frac{w_{s_1}}{v_{s_1}} - \frac{w_{21}}{v_{21}}}{x_2 - x_1}.$$

In the immediate neighbourhood of a plaitpoint  $\frac{w_{21}}{x_2 - x_1}$  and  $\frac{v_{21}}{x_2 - x_1}$  is equal to zero, (Cont. II, p. 125); and we find  $\frac{dp}{dT} = \left( \frac{\partial p}{\partial T} \right)_x$ .

One more remark to conclude with. Now that we have concluded to the existence of the tops of the curves  $V_{sf} = 0$  and  $W_{sf} = 0$ , we shall also have to accept the conclusion, that the complications in the course of the  $(p, x)$  and the  $(p, T)$  sections of the surface of fluid phases coexisting with solid ones, remain restricted to the neighbourhood of the critical phases. It is therefore uncertain, whether in a section for given  $x$ , if the latter is e.g. chosen halfway between  $x_c$  and  $x_n$ , the two vertical tangents still occur. As soon as they have coincided, the section has no longer any special point, and so the retrograde solidification has also disappeared.

**Mathematics.** — “*Centric decomposition of polytopes.*” By Prof. P. H. SCHOTTE.

In the following lines it will be shown how a regular polytope can be decomposed according to its vertices or to its limiting spaces of the greatest number of dimensions into a system of congruent regular polytopes with a common centre. For this  $P_{m,n}^{(r)}$  shall represent a regular polytope, limited by  $m$  spaces  $S_{n-1}$  in  $S_n$ , with a length  $r$  of the edges; and moreover we shall omit as much as possible the number  $n$  of the dimensions and always each of the predicates “regular”, “congruent” and “concentric”.

In our space the theorems hold good:

I<sup>a</sup>. "The eight vertices of a cube  $P_6^{1/2}$  can be arranged into two quadruples of vertices not connected by edges, or of non-adjacent vertices, the vertices of two tetraeders  $P_4^{(V^2)}$ ."

I<sup>b</sup>. "The eight faces of an octaeder  $P_8^{(1)}$  can be arranged into two quadruples of planes of which no two planes pass through one and the same edge, i. e. of quadruples of non-adjacent planes, the faces of two tetraeders  $P_4^{2/}$ ."

II<sup>a</sup>. "The twenty vertices of a  $P_{12}^{(1)}$  form taken *twice* the vertices of five  $P_6^{1,1+V^5}$  and taken *once* in two different ways the vertices of five  $P_4^{1,1+V^5,V^2}$ ."

II<sup>b</sup>. "The twenty faces of a  $P_{20}^{(1)}$  form taken *twice* the faces of five  $P_8^{1,3+V^5,V^2}$  and taken *once* in two ways the faces of five  $P_4^{1,3+V^5,V^2}$ ."

The length of the edges indicated for the components follows immediately from the observation that for the decomposition according to the vertices the radius of the circumscribed sphere, for the decomposition according to the faces the radius of the inscribed sphere remains unchanged.

For  $S_4$  we have the following theorems:

III. "The sixteen vertices of a  $P_8^{(1)}$  can be arranged into two octuples of non-adjacent vertices, the vertices of two sixteen-cells  $P_{16}^{(V^2)}$ . In like way  $P_{16}^{(1)}$  gives according to the limiting spaces two  $P_8^{1/2V^2}$ ."

IV. "The twenty-four vertices of a  $P_{24}^{(1)}$  form the three octuples of vertices of three  $P_{16}^{(V^2)}$ . In like way  $P_{24}^{(1)}$  gives according to the limiting spaces three  $P_8^{(V^2)}$ ."

V. "The one hundred and twenty vertices of a  $P_{60}^{(1)}$  form in five different ways the vertices of five  $P_{24}^{[1(1+V^5)]}$ . In like way  $P_{120}^{(1)}$  gives according to the limiting spaces in five ways five  $P_{24}^{1/4(7+3V^5)V^2}$ ."

VI. "The six hundred vertices of a  $P_{120}^{(1)}$  form in two different ways the vertices of five  $P_{600}^{(1+1/5, 1/2)}$ . In like way  $P_{600}^{(1)}$  gives in two ways the limiting spaces of five  $P_{120}^{(1/5, 1/2)}$ ."

With the aid of these theorems it is easy to arrive at the remaining possible centric decompositions of the four-dimensional polytopes.

In spaces with a greater number of dimensions it is known that but three regular polytopes are to be found, i. e. in  $S_n$  the simplex  $P_{n+1}$ , the polytope of measure  $P_{2n}$  and the polytope  $P_{2^n}$  reciprocally related to the preceding. With respect to these there is an extension for theorem I and theorem III only, namely I for  $n = 2^p - 1$  and III for  $n = 2^p$ . These extensions run as follows:

VII. "In space  $S_{2^p-1}$  the  $2^{2^p-1}$  vertices of a  $P_{2(2^p-1)}^{(1)}$  form the vertices of  $2^{2^p-1}$  simplexes  $P_{2^p}^{[V_{2^p-1}]}$ . In like way a  $P_{2^p-1}^{(1)}$  gives according to the limiting spaces of  $2^p - 2$  dimensions  $2^{2^p-1}$  simplexes  $P_{2^p}^{[V_{2^p}]}$ ."

VIII. "In space  $S_{2^p}$  the  $2^{2^p}$  vertices of a  $P_{2^p+1}^{(1)}$  from the vertices of  $2^{2^p-1}$   $P_{2^p}^{[V_{2^p-1}]}$ . In like way a  $P_{2^p+1}^{(1)}$  gives according to the limiting spaces of  $2^p - 1$  dimensions  $2^{2^p-1}$   $P_{2^p+1}^{[V_{2^p-1}]}$ ."

In the meeting of June 27, 1903 Prof. J. M. VAN BEMMELEN communicated a paper: "*On absorption compounds which may change into chemical compounds or solution.*"

(This paper will not be published in these Proceedings.)

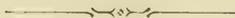
Koninklijke Akademie van Wetenschappen  
te Amsterdam.

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# PROCEEDINGS

OF THE

SECTION OF SCIENCES.



VOLUME VI.

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# C O N T E N T S.

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	Page.
Proceedings of the Meeting of December 19 1903 . . . . .	369
» » » » January 30 1904 . . . . .	451
» » » » February 27 » . . . . .	599
» » » » March 19 » . . . . .	659
» » » » April 23 » . . . . .	737

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

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PROCEEDINGS OF THE MEETING  
of Saturday December 19, 1903.

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C O N T E N T S.

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E. F. VAN DE SANDE BAKHUYZEN: "Investigation of the errors of the tables of the moon of HANSEN—NEWCOMB for the years 1895—1902", p. 370.

J. P. KUENEN: "On the critical mixing-point of the two liquids". (Communicated by Prof. J. D. VAN DER WAALS), p. 387.

C. WINKLER and G. VAN RIJNBERG: "Something concerning the growth of the lateral areas of the trunkdermatomata on the caudal portion of the upper extremity", p. 392.

A. P. N. FRANCHIMONT presents the dissertation of Dr. F. M. JAEGER: "Crystallographic and molecular symmetry of position isomeric benzene derivatives", p. 406.

H. W. BAKHUIS ROOZEBOOM: "The sublimation lines of binary mixtures", p. 408.

A. F. HOLLEMAN and G. L. VOERMAN: "A quantitative research concerning BAEYER's tension theory", p. 410.

E. F. VAN DE SANDE BAKHUYZEN: "Investigation of the errors of the tables of the moon of HANSEN—NEWCOMB in the years 1895—1902" (2nd Paper), p. 412. — (2nd Paper, part II), p. 422.

C. SANDERS: "Contributions to the determination of geographical positions on the West-coast of Africa" (II). (Communicated by Dr. E. F. VAN DE SANDE BAKHUYZEN), p. 426.

G. VAN DIJK and J. KUNST: "A determination of the electrochemical equivalent of silver". (Communicated by Prof. H. HAGA), p. 441.

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The following papers were read:

**Astronomy.** — “*Investigation of the errors of the tables of the moon of HANSEN—NEWCOMB for the years 1895—1902*”. By Dr. E. F. VAN DE SANDE BAKHUIJZEN.

(Communicated in the meeting of June 27, 1903).

### *I. Introduction.*

1. In the years 1901—1902 Mr. C. SANDERS has made a longitude determination on the West-coast of Africa by means of the moon. The investigation described in the following pages was undertaken in order to furnish him with accurate data for the moon's places.

Especially with regard to the systematic errors which affect all the observations of the moon's limbs, it is desirable to use for this purpose not only a few observations made in the neighbourhood of the days for which the places of the moon are required, but to make a more extensive investigation of the errors of the tables. There was still another reason for doing so. For when I first undertook the work, for which the observations at Greenwich had to form the basis, I could dispose only of those up to the year 1899, so that a direct determination of the required corrections was entirely impossible.

So at first I employed only the observations of the years 1895—1899, but later I was able to extend my investigation also over the 3 following years. For this I am indebted to the courtesy of Mr. CHRISTIE, who sent me a complete copy of the observations of the moon made at Greenwich during the years 1900—1902 and who thus enabled me to render my results much more reliable. In the same letter, however, Mr. CHRISTIE told me that a similar investigation for a similar purpose had been undertaken at Greenwich <sup>1)</sup> and at first this made me doubt whether in this circumstance it would not be better to stop my work. But as my calculations for the period 1895—1899 were rather far advanced, I ultimately resolved to continue them. I considered that perhaps in this case it might be useful when two independent investigations should confirm each other.

2. It is well-known that the motion of the moon offers many unsolved problems. Quite recently NEWCOMB in a paper read at the March-meeting of the English Royal Astronomical Society <sup>2)</sup>, (when I had already begun my work), once more clearly pointed out the deficiencies of the theory which chiefly his investigations had brought to light. Let us shortly recapitulate those investigations.

<sup>1)</sup> Comp. Report of the Astronomer Royal . . . read 1903 June 6, p. 9.

<sup>2)</sup> Monthl. Not. R. Astr. Soc. Vol. 63, p. 316.

In 1876 NEWCOMB published a comparison of the observations of the moon from 1862—1874 with the tables of HANSEN<sup>1)</sup> and showed the existence of slowly increasing errors in the tabular mean longitude. On the other hand, after having applied theoretical corrections to the coefficients of some of HANSEN's inequalities of short period, he found a hitherto unsuspected inequality in the true longitude of the form  $a \sin (g + N)$ , where  $g$  represents the mean anomaly and  $N$  an angle increasing by about  $20^\circ$  per annum. The long period errors were further investigated by NEWCOMB in his *Researches*<sup>2)</sup>, which appeared in 1878. After an elaborate investigation of all the observations before 1750, he embodied the errors found in an empirical formula, which apparently satisfied all the available observations.

In the same year he published his "*Corrections to HANSEN's tables of the moon*", where tables were given for the application of the long period corrections according to the empirical formula alluded to above and for the correction of a term of the true longitude accidentally introduced into the tables with a wrong sign. For the time being he did not consider it advisable to apply other corrections. These "*Corrections*" have since been introduced into all the lunar ephemerides.

For the empirical term of long period no theoretical basis has been found until now. As for the term depending on  $g + N$ , NEISON's and HILL's investigations have shown that it may be the "*Jorian Erection*".

## II. Investigation of the errors of longitude.

3. In my investigation I followed the same method as NEWCOMB in his paper of 1876, that is to say, instead of the errors of longitude and latitude I used those of right ascension and declination. Although in this way the calculations become somewhat more intricate, it offers the great advantage that the errors of observation, the systematic and the chance errors, in the two coordinates do not become intermixed.

Thus in investigating the errors of longitude, I started from the differences  $\Delta \alpha$ , which, in accordance with NEWCOMB I take in the sense: Computation—Observation.

4. In the first place I had to investigate the systematic errors in the observed transits of the two limbs, but, as it is well-known, the values found for them depend to a high degree on the value adopted for the parallactic inequality. This renders an independent determination of the two very difficult, as, for instance, it may be

<sup>1)</sup> S. NEWCOMB, Investigation of corrections to HANSEN's tables of the moon with tables for their application. Washington 1876.

<sup>2)</sup> S. NEWCOMB, Researches on the motion of the moon. Washington 1878.

seen from an examination of NEWCOMB'S elaborate investigation, laid down in his "*Astronomical constants*" p. 148—151.

Therefore I thought it best to leave out an independent determination of the coefficient of the parallactic inequality. For in the first place the investigations of the last years have yielded a value of the solar parallax that must be pretty accurate and in the second place the direct determinations of the parallactic inequality that are entirely or partly free from the disadvantage mentioned, namely those of BATTERMANN<sup>1)</sup> from occultations observed at Berlin and those of FRANZ<sup>2)</sup> from transit observations of the crater MÖSTING A made at Königsberg, give results which agree satisfactorily with the most probable value of the solar parallax.

Whilst as this most probable value we may consider  $\pi = 8''.796$ , the investigations of BATTERMANN and FRANZ yield:

BATTERMANN 1884—85	$\pi = 8''.794$
"    1894—96	8.775
FRANZ 1892	8.770 <sup>3)</sup>

On the other hand NEWCOMB derived from the transit observations of the limbs by eliminating as far as possible the systematic errors:

$$\text{NEWCOMB 1862—94} \quad \pi = 8''.802.$$

I have adopted  $\pi = 8''.796$ , hence as the correction of the value used ultimately by HANSEN in the *Tables de la Lune*:  $\delta \pi = -0''.120$ , whence as correction of the coefficient of the principal term of the parallactic inequality in the mean longitude:

$$\delta P = -14.10 \times \delta \pi = +1''.69$$

and  $P = -124''.01$

The correction of the value adopted by NEWCOMB becomes:

$$\delta P = +0''.73.$$

5. I now proceeded as follows. The residuals  $\Delta \alpha$  for each year were arranged according to the observed limb and the true age of the moon expressed in days. In this way each year yielded 25 groups of residuals and for each of them the mean value was derived.

<sup>1)</sup> H. BATTERMANN, Beobachtungs-Ergebnisse der Sternwarte zu Berlin No. 5. Berlin 1891.

H. BATTERMANN, Beobachtungs-Ergebnisse der Sternwarte zu Berlin No. 11. Berlin 1902.

<sup>2)</sup> Astron. Nachr. Bd. 136. p. 254.

<sup>3)</sup> I had overlooked the discussion by FRANZ of the observations of MÖSTING A made at GÖTTINGEN 1891—93 (*Astron. Nachr.* Vol. 144 p. 177). The combined result from KÖNIGSBERG and GÖTTINGEN is:  $\pi = 8''.805$ . (*Added 1903 Dec.*)

These annual means for each day of the moon's age had then to be corrected 1<sup>st</sup> for the correction of the parallactic inequality, 2<sup>nd</sup> for the small theoretical corrections derived by NEWCOMB on p. 10 of his "*Investigation*". However, for these annual means some of the latter might be neglected and besides I might identify annual means of  $\Delta \alpha$  with those of the residuals in mean longitude and also annual means of the true age with those of the mean age, the argument  $D$ .<sup>1)</sup>

For the years 1895—97 I had at my disposal not only the results of the transit observations, but also those obtained with the altazimuth. As however in this case the advantage of also using observations made at small elongations is more than balanced by the difficulty of determining their systematic errors, I have ultimately only used the transit observations<sup>2)</sup>.

From these corrected means, which are not given here, I further derived mean values for each year for each of the two limbs. They were obtained by combining with equal weights the results for each day of the age of the moon. However, for reasons to be given hereafter, the values for the ages of 4 and 26 days were ultimately rejected altogether.

In this way I found:

	$\Delta \alpha$ I	$\Delta \alpha$ II	II — I	$\frac{I + II}{2}$
1895	— 0.062	— 0.072	— 0.010	— 0.067
1896	— 0.131	— 0.044	+ 0.087	— 0.088
1897	— 0.134	— 0.126	+ 0.008	— 0.130
1898	— 0.177	— 0.104	+ 0.073	— 0.140
1899	— 0.125	— 0.070	+ 0.055	— 0.098
1900	— 0.151	— 0.104	+ 0.047	— 0.128
1901	— 0.144	— 0.091	+ 0.053	— 0.118
1902	— 0.189	— 0.123	+ 0.066	— 0.156
Mean			+ 0.047	

1) The corrections actually applied were the annual means for each value of  $D$  of the values of NEWCOMB's Table VII, after they had been corrected for the adopted value of the principal term of the parallactic inequality.

2) At first I had also used the altazimuth observations and from results obtained on the same day with both instruments I had derived for  $\Delta \alpha_A - \Delta \alpha_T$  for observations of the 1<sup>st</sup> limb + 0.126, and for those of the 2<sup>nd</sup> limb — 0.122.

By subtracting these annual means for each limb as they are given in the second and third columns of the table above from the means for the same limb for each day of the moon's age I obtained for each year a set of about 25 residuals and finally I combined the corresponding residuals of the 8 years with their respective weights.

These mean residuals follow here :

Limb I			Limb II		
Age	$\delta \Delta z$	Weight	Age	$\delta \Delta z$	Weight
4	- 0.121	12	14	- 0.027	14
5	- .069	32	15	- .065	33
6	- .022	36	16	+ .023	61
7	- .036	41	17	+ .030	49
8	+ .022	50	18	- .009	53
9	+ .007	46	19	+ .048	45
10	+ .002	43	20	+ .008	34
11	+ .011	50	21	+ .003	31
12	+ .011	54	22	+ .013	37
13	+ .029	49	23	+ .017	38
14	+ .007	49	24	- .015	31
15	.000	27	25	+ .008	19
			26	+ .126	8

If we assume the adopted values for the inequalities depending on  $D$  to be correct, the two preceding tables show us the effect of the systematic errors of the observations. At a first glance at the second table we perceive that the right ascensions observed at the age of 4 and 26 days show abnormally great discordances, which both agree in sign with those which would result if the observers estimated the moon's diameter to be smaller when observed at daylight.

If we except these two groups, the observations of the 2<sup>nd</sup> limb no longer show any regular increase, whilst the results for the 1<sup>st</sup> limb between the ages of 5 and 8 days still seem to vary somewhat regularly. However, after due consideration of the case, I have ultimately assumed the personal error to be constant for the first limb

between the age of 5 and 15 days and for the second limb between those of 14 and 25 days and I simply rejected the observations at the age of 4 and 26 days which are few in number. Perhaps it would have been better to apply a special correction at least to the results at the age of 5 days.

As stated above, the values in the 2<sup>nd</sup> and 3<sup>rd</sup> columns of the first table are those found after the rejection of the two extreme groups, and from them I derived further the differences II—I and the values of  $\frac{1}{2}(I + II)$ . The II—I represent the differences between the personal errors for the two limbs. In the first three years these differences show considerable variations, but for the last five years there is a good agreement. However, as at first I only discussed the period 1895—1899 I adopted a mean value of II—I for these years and another for the following three, and for the corrections to be applied to the observations of the first and the second limbs to reduce them to the mean of the two I assumed for 1895—1899  $\pm 0^s.02$ , for 1900—1903  $\pm 0^s.03$ .

For a closer investigation of the personal errors it would be necessary to discuss separately the results of the different observers.

6. After having applied the corrections for personal error we must now compute for the separate observations the corrections to be applied to the mean longitude: in the first place those resulting from the corrections of the parallactic inequality of the annual equation, of the variation and of the evection — the last three as derived by NEWCOMB — and secondly the long period corrections. From the corrections of the mean longitude we must then derive those of the right ascensions.

The corrections of the first kind (comp. NEWCOMB *Invest.* p. 10 and 37 and BATTERMANN N<sup>o</sup>. 5 p. 21) are, using HANSEN's notations:

$$\begin{aligned} n \delta z = & + 1.''69 \sin D + 0.''16 \sin (D - g) - 0.''24 \sin (D + g') \\ & + 0.''09 \sin g' - 0.''33 \sin 2 D - 0.''21 \sin (2 D - g). \end{aligned}$$

For the application of these corrections I have calculated 2 tables, partly arranged as NEWCOMB's Table VII and VIII.

For the long period corrections I first tried to derive accurate values from the whole available material.

For although the empirical correction derived by NEWCOMB in his *Researches*, has reduced the differences from the observations to a much smaller amount, there still remain unaccounted for discrepancies. This has been shown by TISSERAND in his very lucid account of the questions involved here "Sur l'état actuel de la théorie de la lune" in the 3<sup>rd</sup> volume of his *Mécanique Céleste*. He also showed there that we cannot improve the agreement by altering the

period of the empirical term which NEWCOMB fixed on 273 years.

Hoping to find some indication about the empirical law which would represent the outstanding differences, I put together for the whole period 1847—1902 the values of the mean annual errors in longitude or in R. A. according to the observations at Greenwich. Those as far as 1882<sup>1)</sup> were borrowed from STONE's papers in the *Monthl. Not.*, applying to his results NEWCOMB's corrections, while those for the subsequent years were taken from the Annual Reports of the Astronomical Society. To all these results the small corrections were applied for the reduction of the observations to the same standard time-star catalogue. As such I adopted the 2<sup>nd</sup> 10 year Catalogue.

I added to the Greenwich results: for the years 1862—1874 NEWCOMB's results which partly depend on the Washington observations, for the years 1880—1892 the results of the observations at Oxford as given by STONE, applying to both NEWCOMB's corrections and for the years 1895—1902 the results derived from the Greenwich observations by myself ( $\frac{1}{2}$  (I + II) in the first table of section 5). From a comparison of the results of different observatories for the same year we may infer that they are tolerably accurate. The differences between my results and those computed at Greenwich range from 0."00 to 0."36.

I do not, however, give these annual mean errors here, as I did not succeed in deriving anything from them with certainty. By assuming the existence of a new inequality with a period of about 50 years with maxima about 1862 and 1887 and a coefficient of about 3" we should attain a somewhat better, but even then not an absolute agreement.

So the only thing I could do to obtain the mean corrections required for my purpose, was to represent the annual mean errors from 1886—1902 by a smooth curve. The following values were derived from it.

1895.0	$\delta\lambda = +$	0"53
1896.0		1.06
1897.0		1.44
1898.0		1.72
1899.0		1.93
1900.0		2.09
1901.0		2.21
1902.0		2.28
1903.0		2.30

<sup>1)</sup> For the years 1847—1861 the new reduction of the Greenwich observations of the moon (*Monthl. Not.* Vol. 50) was used.

Obviously the last values cannot be very certain.

After thus having formed the total corrections to be applied to the mean longitude, they have been reduced to corrections of the right ascensions. For this reduction I could use the values  $F$  and  $(v. a)$  given by NEWCOMB in his Table IX and XI. The very small reduction from orbit longitude to ecliptic longitude could be neglected. (Comp. also *Investigation* p. 12 and 14).

7. The  $\Delta a$  corrected in this way were now used to derive from them the corrections of the true longitude, which depend on the sine and cosine of the mean anomaly. In his *Investigation* p. 16 NEWCOMB has shown that for this purpose we may use instead of the residuals of true longitude those of right ascension and although the error of the longitude of the node which is assumed to be small has increased since 1868, his conclusion still holds.

For each year the  $\Delta a$  were arranged in 18 groups according to the values of the mean anomaly, the first group containing those between  $g = 0^\circ$  and  $20^\circ$ , the second those between  $g = 20^\circ$  and  $40^\circ$  etc. Then the sums and the means for each group were formed and were regarded as corresponding to  $g = 10^\circ$ ,  $g = 30^\circ$  etc. just as had been done by NEWCOMB.

If we represent the corrections which are to be applied to the true longitude of HANSEN by

$$\delta l = -h \sin g - k \cos g$$

we obtain for each year 18 equations of the form

$$c + h \sin g + k \cos g = r$$

where  $c$  is the outstanding mean error of longitude, whilst for  $h$  and  $k$  the signs are in accordance with NEWCOMB.

The equations were solved for each year by least squares with due regard to the weights of  $r$ , which were assumed to be proportional to the number of observations used.

So I obtained the following values of  $h$  and  $k$ :

	$h$	$k$
1895.5	+ 0"29	+ 0"44
1896.5	+ 0.66	+ 1.16
1897.5	+ 0.57	+ 1.77
1898.5	+ 0.51	+ 2.10
1899.5	- 0.93	+ 2.83
1900.5	- 1.66	+ 1.12
1901.5	- 1.46	+ 0.52
1902.5	- 1.18	+ 0.01

It is obvious that these coefficients cannot result from errors in the

excentricity and the longitude of the perigee only, and their periodic character fully confirms the existence of the inequality discovered by NEWCOMB.

At a closer inspection, however, it appears that NEWCOMB'S formula does not represent satisfactorily my  $h$  and  $k$ , and this need not astonish us if we consider the great extrapolation involved in the application of NEWCOMB'S formula to my results.

8. To correct NEWCOMB'S formula by successive approximations I have proceeded in the following way:

By comparing the  $h$  and  $k$  now obtained with those in the table in *Investigation* p. 28, it may be easily seen that the period of the argument  $N$ , on which  $h$  and  $k$  depend through the formulæ  $h = h_c - a \sin N$  and  $k = k_c + a \cos N$ , must be greater than  $16\frac{2}{3}$  years — the period assumed by NEWCOMB — and cannot differ much from 18 years. This corresponds to an annual variation of  $20^\circ$  and it will be convenient to adopt this value as a first approximation.

The special aim of my first operation was to find reliable values for the constant parts of the coefficients,  $h_c$  and  $k_c$ . I tried to attain this by calculating values of  $h$  and  $k$  for each year of the 18 year-cycle by means of the results of NEWCOMB'S two series and of those found for 1895—1902.

Assuming the argument for  $1862.0 \pm n \times 18$  to be 0, I derived normal values for the arguments 0.5, 1.5 etc. to 17.5, assigning the weights 1, 3 and 2 to the results of the 3 series. I had no value for the argument 14.5 and therefore had to form it by interpolation.

In this way I found:

Arg.	$h$	$k$	Arg.	$h$	$k$
0.5	+ 0 <sup>u</sup> 23	+ 1 <sup>u</sup> 58	9.5	+ 1 <sup>u</sup> 51	— 0 <sup>u</sup> 74
1.5	— 0.76	+ 2 20	10.5	+ 1.97	— 0.45
2.5	— 1.31	+ 1.10	11.5	+ 1.67	+ 0.09
3.5	— 1.20	+ 0.12	12.5	+ 1.79	+ 0.77
4.5	— 0.69	— 0.06	13.5	+ 0.80	+ 1.24
5.5	— 0.79	— 0.68	14.5	+ 0.80	+ 0.84
6.5	+ 0.20	— 1.57	15.5	+ 0.29	+ 0.44
7.5	+ 1.21	— 1.68	16.5	+ 0.66	+ 1.16
8.5	+ 1.20	— 1.46	17.5	+ 0.57	+ 1.77

From these values formulae were derived, which after a transformation in order to bring the zero-epoch on 1868.5 become:

$$\begin{aligned} h &= + 0''.45 - 1''.30 \sin [167^\circ.1 + 20^\circ (t-1868.5)] \\ k &= + 0''.26 + 1''.46 \cos [149^\circ.3 + 20^\circ (t-1868.5)]. \end{aligned}$$

If we assume that the amplitude and the argument of the two periodic terms must be equal, the formulae become:

$$\begin{aligned} h &= + 0''.45 - 1''.37 \sin [157^\circ.7 + 20^\circ (t-1868.5)] \\ k &= + 0''.26 + 1''.37 \cos [157^\circ.7 + 20^\circ (t-1868.5)]. \end{aligned}$$

The object of the second operation was to derive from the observations 1895—1902 the most reliable value of  $N$  for the middle-epoch, assuming its annual variation to be  $20^\circ$ . Starting from the  $8 \times 18$  values of  $r$  and assuming as known only the values of  $c$ , (as found from the solution of the equations for each year) and those of  $h_c$  and  $k_c$  (as found above), I first subtracted the  $c$  from the  $r$  and then freed the latter from the influence of  $h_c$  and  $k_c$ .

The residuals must then be of the form:

$$r' = -a \sin N \sin g + a \cos N \cos g = a \cos (g + N_0 + t \times 20^\circ)$$

and now it is clear that the  $8 \times 18$  residuals correspond with only 18 different values of the argument  $N_0 + g + t \times 20^\circ$ . Consequently these residuals could be combined in 18 values, for instance the  $r'$  for  $g=10^\circ$  in 1895 could be combined with that for  $g=350^\circ$  in 1896, with that for  $g=330^\circ$  in 1897 etc.

Having due regard to the weights, the following mean values of  $r'$  were derived. The arguments  $g$  hold for 1898 i.e. for 1898.5.

$g$	$r'$	$g$	$r'$	$g$	$r'$
10°	+ 1''61	130°	- 1''32	250°	+ 0''13
30	+ 1.68	150	- 1.29	270	+ 0.04
50	+ 0.65	170	- 1.31	290	+ 0.62
70	+ 0.23	190	- 1.05	310	+ 1.27
90	- 1.12	210	- 1.09	330	+ 1.66
110	- 1.17	230	- 0.77	350	+ 1.48

These values are represented by the formula:

$$- 0''.42 \sin g + 1''.51 \cos g = + 1''.57 \cos (g + 15^\circ.5).$$

and  $15^\circ.5$  will be a pretty accurate normal value of  $N$  for 1898.5. For the derivation of a similar normal value from each of the two series of NEWCOMB I chose a less direct but simpler method. In each series I reduced the  $N$  derived from each year to a mean epoch by means of the annual variation  $20^\circ$  and then combined them with the weights as given by NEWCOMB<sup>1)</sup>. I did not however use the  $N$  of

<sup>1)</sup> Applying the same method to the observations 1895—1902 I should have found for  $N_0$   $16^\circ.9$  instead of  $15^\circ.5$ .

NEWCOMB, but the slightly modified values, which were obtained by taking  $h_c = + 0''.45$  and  $k_c = + 0''.26$ .

The three normal values obtained thus were:

1852.6	$N = 200.7$	Weight 1	$O. - C. - 9^\circ 0$
1868.5	161.9 <sup>1)</sup>	3	+ 4.6
1898.5	15.5	2	- 2.3

and from them I derived a corrected formula for  $N$ ; I found:

$$N = 157^\circ.3 + 19^\circ.35 (t - 1868.5)$$

or taking the mean year as zero-epoch

$$N = 302^\circ.4 + 19^\circ.35 (t - 1876.0).$$

The outstanding differences Obs.—Comp. are given above.

If I had assigned equal weights to the three normal values, I should have found for the annual motion  $19^\circ.45$ , while by excluding the first I should have found  $19^\circ.12$ , both differing only slightly from the most probable value.

At first when NEWCOMB's value for the annual variation of  $N$  appeared to be too large I had thought that the true value might be equal to the theoretical annual variation of the argument of the Jovian Evection, i. e.  $20^\circ.65$ . It appears, however, that even the latter is too large to satisfy the observations.

To judge in how far this is the case a comparison is given below of the values of  $N$  for each year as directly derived from observations, first with my formula, secondly with the formula we obtain if we assume the same value of  $N$  for 1876.0, but take as annual variation  $20^\circ.65$ . The two sets of differences are given under the headings  $N_O - N_C$  and  $N_O - N_J$ .

<i>Epoch</i>	<i>Weight</i>	$N_O - N_C$	$N_O - N_J$
1847.8	1	- 56°	- 19°
48.9	3	+ 11	+ 46
50.1	3	+ 2	+ 36
51.2	3	- 22	+ 10
52.4	4	- 30	+ 1
53.5	3	- 30	- 1
54.6	3	- 37	- 9
55.8	0.5	+ 7	+ 33
56.9	3	+ 27	+ 52
58.1	1	+ 101	+ 124

<sup>1)</sup> With NEWCOMB's values of  $N$  we should have found  $200^\circ.5$  and  $161^\circ.7$ .

<i>Epoch</i>	<i>Weight</i>	$N_O - N_C$	$N_O - N_I$
1862.5	3	— 18	0
63.5	5	— 25	— 9
64.5	5	— 19	— 4
65.5	4	+ 7	+ 21
66.5	2	— 19	— 7
67.5	4	— 24	— 13
68.5	4	+ 19	+ 29
69.5	5	+ 37	+ 45
70.5	5	+ 20	+ 27
71.5	3	+ 28	+ 34
72.5	4	+ 22	+ 27
73.5	4	+ 12	+ 15
74.5	4	+ 10	+ 12
1895.5	0.5	+ 82	+ 57
96.5	2	+ 8	— 19
97.5	4	— 3	— 31
98.5	4	— 20	— 49
99.5	6	— 9	— 40
1900.5	4	+ 12	— 20
01.5	4	+ 6	— 27
02.5	4	+ 4	— 30

That the differences, even those with the formula that is made to represent the observations as well as possible, are not altogether accidental, may be seen from the great number of permanencies of sign. Yet I hold that we are entitled to the conclusion that an annual variation of  $N$  of  $19^{\circ}.35$  better represents reality than one of  $20^{\circ}.65$ .

Having thus derived a formula for  $N$  representing as well as possible the results at my disposal, I had still to correct the adopted values of the coefficient  $a$  and of  $h_c$  and  $k_c$ .

To this end I compared the observed values of  $h$  and  $k$  with the formulæ

$$h = + 0''.45 - 1''.50 \sin [302^{\circ}.4 + 19^{\circ}.35 (t - 1876.0)]$$

$$k = - 0''.26 + 1''.50 \cos [302^{\circ}.4 + 19^{\circ}.35 (t - 1876.0)]$$

and formed the outstanding residuals Obs.—Comp. These residuals which for shortness are not given here, were divided into 4 groups according to the 4 quadrants of  $N$ , and for each of these groups mean values were formed which follow here:



while from my formula would follow:

$$1885.0 \quad \delta l = + 0''.99 \sin g + 0''.41 \cos g$$

$$1896.0 \quad \delta l = - 1''.05 \sin g - 1''.49 \cos g$$

Thus we find a very good agreement for 1896.0, but the results for 1885.0 cannot at all be brought to harmonize. It would be very interesting to investigate also the meridian observations of the years about 1885.

The annual variation found for  $N$  agrees in absolute value almost exactly with that of the longitude of the node and we might put for the argument of the inequality:  $g - \theta + 216^\circ$ . It is probable, however, that we have only to do here with a casual agreement.

The theoretical value of the "Jovian Evection" is according to the most accurate calculation by HULL:

$$\delta l = + 0''.90 \sin [g + 238^\circ + 20''.65 (t - 1876.0)].$$

For 1856 the theoretical argument and that of the empirical term are in good agreement, but in the following years they are more and more discordant.

9. It only remains now to put together the final results for the mean corrections of the longitude, as they were derived from the solution of the equations for each year.

In the following table the column headed  $\delta \lambda$  contains the residual corrections found after the corrections derived from my curve had been applied, while the column headed  $\delta \lambda_N$  contains the total corrections to be applied to the longitude of HANSEN-NEWCOMB.

	$\delta \lambda$	$\delta \lambda_N$
1895.5	— 0''07	+ 0''73
96.5	— 0.05	+ 1.21
97.5	+ 0.36	+ 1.95
98.5	+ 0.22	+ 2.05
99.5	— 0.48	+ 1.53
1900.5	— 0.27	+ 1.88
01.5	— 0.46	+ 1.79
02.5	+ 0.16	+ 2.46

The mean value of the  $\delta \lambda$  amounts to — 0''07, which might be applied as a constant correction to the results according to my curve.

These results of the transit observations, which contain the unknown personal errors in observing the moon's limbs may be compared with those of BATTERMANN and also with those derived by FRANZ from the observations of the crater Mösting  $\Delta$ . We then find that the results found by them for the mean longitude for 1885.0, 1896.0 and

1892.5 after being reduced on the system of the 2<sup>nd</sup> 10 year catalogue are greater by  $+0''.6$ ,  $+0''.1$  and  $+0''.5$  respectively than those of the transit observations at Greenwich<sup>1)</sup>.

As to the occultations, it is proved by H. G. v. D. SANDE BAKHUYZEN<sup>2)</sup> that values for the moon's longitude derived from them will generally be too small and therefore it is probable that the moon's longitude according to the observations at Greenwich is still in need of a positive correction.

### III. Investigation of the errors of the latitude.

10. My investigation of the errors of the moon's latitude was based on that of the errors in declination.

First I tried to determine the constant errors in the observations of the moon's declination and to this end I utilized the observations from 1895 to 1899. From the differences  $\Delta \delta = \text{Comp.} - \text{Obs.}$  I derived mean values for each of the two limbs for each month of the year and from them annual means were derived by taking the mean of the monthly means without regard to their weights.

In this way I obtained the results given in the following table. The 2<sup>nd</sup> and 3<sup>rd</sup> columns contain the annual means for the north limb and the south limb, the 4<sup>th</sup> the means of the two, the 5<sup>th</sup> their differences i. e. the errors of the moon's diameter, while the 6<sup>th</sup> contains this same error derived only from simultaneous observations of the two limbs near full moon.

	North	South	$\frac{N+S}{2}$	$N-S$	$(N-S)_f$
1895	$-0''15$	$+0''55$	$+0''20$	$-0''70$	$-0''65$
1896	$-0.15$	$-0.49$	$-0.32$	$+0.34$	$+0.19$
1897	$-0.55$	$+0.29$	$-0.13$	$-0.84$	$-1.57$
1898	$+0.05$	$-0.03$	$+0.01$	$+0.08$	$+0.78$
1899	$+0.35$	$+0.08$	$+0.22$	$+0.27$	$+0.16$
Mean	$-0''09$	$+0''08$	$0''00$	$-0''17$	$-0''22$

<sup>1)</sup> If we combine FRANZ's result from his Königsberg observations with that which he derived from those at Göttingen, which had been overlooked by me, the last difference, instead of  $+0''.5$ , becomes  $+0''.3$  (Added 1903 Dec.)

<sup>2)</sup> H. G. v. D. SANDE BAKHUYZEN: The relation between the brightness of a luminous point and the moments at which we observe its sudden appearance or disappearance. Proc. Acad. Amst. 4. 465.

Although the differences between the results of the separate years seem to be real, I have applied only to the  $\Delta \delta$  derived from observations of the north and the south limb the constant corrections  $+ 0''.1$  and  $- 0''.1$ .

For the observations of 1900—1902 I did not know which limb was observed. While, however, in the preceding years the constant errors appeared to be small and in the mean for the two limbs were found to be  $0''.0$ , I thought myself justified in neglecting them altogether for 1900—1902.

11. In the second place the  $\Delta \delta$  had to be corrected for the errors of longitude.

We find to a sufficient degree of approximation (comp. also *Investigation* p. 31—32<sup>1)</sup>) that the derivative of the declination relatively to the mean longitude is:

$$\begin{aligned} \frac{d\delta}{d\lambda} = & a(1 + e - e \cos 2\lambda) \cos \lambda + b \cos(\lambda - \theta) \\ & + 2ae \cos(2\lambda - \pi) + 2be \cos(2\lambda - \pi - \theta) \end{aligned}$$

where

$$\begin{aligned} a &= \sin \varepsilon &= 0.398 \\ b &= \cos \varepsilon \sin i &= 0.083 \\ c &= \frac{1}{4} \sin^2 \varepsilon &= 0.040 \end{aligned}$$

For our purpose we may neglect the 3<sup>d</sup> and the 4<sup>th</sup> terms; their short periods permit of their influence being regarded as fortuitous. Also the 2<sup>d</sup> term has provisionally been neglected, as its influence<sup>2)</sup>, may easily be accounted for afterwards.

So there only remains the 1<sup>st</sup> term, which has been tabulated by NEWCOMB in his Table XI, and I multiplied it by the total errors of the mean longitude. The errors of the true longitude depending on  $g$ , give rise in  $d\delta$  only to terms of very short and of very long period which could be neglected as being without influence on the results to be derived.

12. The  $\Delta \delta$  corrected in this way were arranged for each year into 18 groups according to the values of the argument of the latitude  $u$ , in the same way as it was done for the  $\Delta \alpha$  according to the values of  $g$ , and then the sums and the means for each group were formed.

I do not give here these annual means, but only the general means derived from the total sums.

1) In the formula on p. 32  $3eK$  and  $3eH$  ought to be  $2eK$  and  $2eH$ .

2) This term is the influence of the error in longitude on the latitude and consequently directly influences the determination of the longitude of the node, but not that of the inclination.

$u$	$\Delta \delta$	$u$	$\Delta \delta$
10°	+ 0.67	190°	- 0.93
30	+ 0.70	210	- 0.57
50	+ 1.11	230	- 0.42
70	+ 0.75	250	- 0.06
90	+ 0.81	270	0.00
110	- 0.11	290	+ 0.39
130	- 0.01	310	+ 0.58
150	- 0.54	330	+ 1.05
170	- 1.11	350	+ 0.81

Each of the mean residuals gives an equation of condition :

$$\Delta \delta = - 0.96 \sin (\lambda - \theta) \delta i + 0.96 \cos (\lambda - \theta) i \delta \theta$$

where  $\delta i$  and  $\delta \theta$  represent the corrections to the inclination and the longitude of the node. As the  $\Delta \delta$  may still contain an outstanding constant error, the equations were actually put in the form :

$$\Delta \delta = a + b \sin (\lambda - \theta) + c \cos (\lambda - \theta).$$

These equations were solved substituting in them, 1<sup>st</sup> the mean results of the years 1895—1898, 2<sup>d</sup> those of 1899—1902, 3<sup>d</sup> those of the 8 years combined (in all cases the mean results as derived from the total sums).

In this way we obtained :

	$b$	$c$	$c$ corrected
1895—1898	- 0.25	+ 1.11	+ 1.23
1899—1902	+ 0.62	+ 0.63	+ 0.79
1895—1902	+ 0.18	+ 0.86	+ 1.00

The last column contains the values of  $c$  corrected for the influence of the 2<sup>d</sup> term of  $\frac{d\delta}{d\lambda}$ . The corrections actually applied are its products with the mean corrections of the longitude.

The two partial results do not agree very well, especially those for  $b$ , or for the correction of the inclination, and if we compare the corresponding values of  $\Delta \delta$  from the two four-year groups, systematic differences between the two sets are clearly shown. Considering however my results in connection with those of NEWCOMB there seems to be as yet no sufficient ground to assume a periodic part in the coefficients  $b$  and  $c$ .

From the 8 years combined we derive :

$$\begin{aligned} \delta i &= - 0.19 \\ i \delta \theta &= + 1.04 \\ \delta \theta &= + 11.5 \end{aligned}$$

13. Finally we may combine our results with those of NEWCOMB and also with those derived by FRANZ.<sup>1)</sup>

For the correction of the inclination we find :

NEWCOMB	1868	$\delta i = -0''15$	weight 3
FRANZ	1892	+ 0.37	1
BAKH.	1899	- 0.19	3
Mean result		$\delta i = -0''09$	

The correction of the inclination is thus found to be small.

For the correction of the longitude of the node we find :

NEWCOMB	1868	$\delta \theta = +4''5$	weight 3
FRANZ	1892	+ 7.4	1
BAKH.	1899	+ 11.5	3
Mean result	1885	$\delta \theta = +7''9$	

As NEWCOMB found for 1710  $\delta \theta = -16''$  (*Researches* p. 273), we obtain :

Correction of the centennial motion = + 14''.

**Physics.** — “*On the critical mixing-point of two liquids*”. By J. P. KUENEN. (Communicated by Professor VAN DER WAALS in the meeting of October 31, 1903).

A critical mixing-point of two liquids is in general a point where two coexisting liquids become identical in every respect: it corresponds to a plaitpoint or critical point of the two-liquid plait on VAN DER WAALS'S  $\psi$ -surface or of its projection in the volume-composition diagram, the so-called saturationcurve for the two liquid phases; the term is used more especially to denote the condition, where the liquids are at the same time in equilibrium with their saturated vapour. In the  $v$ — $v$  diagram this condition corresponds to the point of contact between the two-liquid curve in its critical point with the vapour-liquid curve: in this condition a change of temperature will either make the critical point appear outside or disappear inside the vapour-liquid curve. The contact sometimes takes place on the inside of the latter curve and the two-liquid curve then lies entirely in the metastable and unstable parts of the diagram, or it lies outside in the stable part of the figure. In other cases it is the vapour curve the critical point of which comes into contact with a two-liquid curve, but whatever the case may be, the geometrical conditions are the

<sup>1)</sup> The combined results of FRANZ from the observations at Königsberg and at Göttingen have been considered in my second paper. (*Added* Dec. 1903).

same and the conclusions to be derived from these must hold good in general.

For the sake of clearness we will consider a special case, viz. that in which the liquid curve falls outside the vapour curve and the contact takes place in the critical point of the former. As the saturation curves contract on heating, the two curves will in this case separate when the temperature is raised above the critical temperature; on the other hand the liquid curve begins to intersect the vapour curve when the temperature is lowered. The relative position of the curves here assumed is very common: it was discovered for the first time by VAN DER LEE for mixtures of phenol and water<sup>1)</sup>.

When the liquid curve intersects the vapour-liquid curve an equilibrium between a vapour phase and two liquid phases is possible, but VAN DER WAALS<sup>2)</sup> has shown how this equilibrium may be ignored and a continuous vapour-liquid curve traced out through the metastable and unstable parts of the diagram: along this curve the liquid phase passes twice through the spinodal curve of the two-liquid curve and at the same moments the vapour branch of the curve forms cusps; the vapour pressure considered as a function of the composition of the liquid passes at the same time through a maximum or minimum; the thermodynamical condition in these points is  $\left(\frac{\partial^2 \zeta}{\partial v^2}\right)_p = 0$ , where  $\zeta$  is the thermodynamical potential.

In many cases the further complication arises that there is a condition, where the compositions of the liquid and the vapour,  $x_1$  and  $x_2$ , are the same and where therefore the pressure is again a maximum or minimum: if this point falls, as it often does, between the two points where  $\frac{\partial^2 \zeta}{\partial v^2} = 0$ , it can only be a minimum and both the other points are then maxima; the composition of the vapour in the three-phase equilibrium then lies between the compositions of the liquids and the three-phase pressure is higher than the pressure of neighbouring mixtures on both sides. This is the case which was assumed by VAN DER LEE in drawing his diagrams for phenol and water, but from subsequent measurements by SCHREINEMAKERS<sup>3)</sup> it appears that for these mixtures the maximum where  $x_1 = x_2$  lies outside the three-phase triangle in the  $v-x$  diagram.

As the temperature approaches the critical point, where the two

1) VAN DER LEE, Dissertatie, Amsterdam 1898. Zeitschr. Physik. Chemie 33 p. 622.

2) VAN DER WAALS. Continuität II, p. 18, fig. 3.

3) SCHREINEMAKERS, Zeitschr. Physik. Chemie, 35, p. 461.

saturation curves separate, the two liquid phases approach each other and finally coincide in the critical point: what becomes of the minimum ( $x_1 = x_2$ ) during this change, if we suppose such a point to lie inside the three-phase triangle? The simplest supposition which we can make is that up to the last moment the minimum remains between the two maxima and thus a fortiori between the coexisting liquids; on that supposition the various points would all coincide in the critical point and unite into one maximum; in the critical point we should then have the condition  $x_1 = x_2$ , i. e. the liquid in the critical point would have the same composition as the vapour with which it is in equilibrium. This assumption was made as almost self-evident by myself<sup>1)</sup> as well as by VAN DER LEE<sup>2)</sup>, but on fuller consideration it now appears to me to be incorrect; VAN DER LEE<sup>3)</sup> tried to prove its correctness by the aid of the thermodynamical relations for binary mixtures, but we shall show that the proof was not valid.

The equation to be used is the following :

$$\frac{dp}{dx_1} = \frac{x_2 - x_1}{v_{21}} \left( \frac{\partial^2 \xi_1}{\partial x_1^2} \right)_p;$$

introducing into this the condition  $\frac{\partial^2 \xi_1}{\partial x_1^2} = 0$ , which defines the spinodal curve and thus holds a fortiori in the critical point, we obtain the equation  $\frac{dp}{dx_1} = 0$ : but it does not follow from this that the vapour pressure has a maximum value; for it may be proved that not only the first differential coefficient  $\frac{dp}{dx_1}$ , but also the second  $\frac{d^2 p}{dx_1^2}$  disappears.

Calculating the value of  $\frac{d^2 p}{dx_1^2}$  from  $\frac{dp}{dx_1}$  we find :

$$\frac{d^2 p}{dx_1^2} = \frac{x_2 - x_1}{v_{21}} \frac{d}{dx_1} \left( \frac{\partial^2 \xi_1}{\partial x_1^2} \right)_p + \frac{1}{v_{21}} \left( \frac{dx_2}{dx_1} - 1 \right) \left( \frac{\partial^2 \xi_1}{\partial x_1^2} \right)_p - \frac{1}{v_{21}^2} \frac{dv_{21}}{dx_1} (x_2 - x_1) \left( \frac{\partial^2 \xi_1}{\partial x_1^2} \right)_p;$$

but in the point of contact of the two curves we have not only  $\left( \frac{\partial^2 \xi_1}{\partial x_1^2} \right)_p = 0$ , but at the same time  $\frac{d}{dx} \frac{\partial^2 \xi}{\partial x_1^2} = 0$ , because the spinodal curve of the two-liquid curve touches the connodal curve of the vapour-liquid curve in the critical point of contact; thus as none of

1) KUENEN en ROBSON, Phil. Mag. (5) 48 p. 184, fig. 2.

2) VAN DER LEE, l. c. p. 69.

3) VAN DER LEE, l. c. p. 74.

the coefficients in the above expression become infinite, all the terms vanish and  $\frac{\partial^2 p}{\partial v_1^2} = 0$ . In the critical point the pressure is in general not a maximum, but the vapour branch of the saturation curve in the  $p-v$  diagram ( $t = \text{constant}$ ) has a point of inflexion with a tangent parallel to the  $v$ -axis.

In a special case VAN DER LEE's conclusion drawn from the equation becomes valid, viz. when in the critical point the condition  $x_1 = x_2$  is fulfilled; for in that case the next differential coefficient  $\frac{d^3 p}{dx_1^3}$  becomes 0, as well as  $\frac{dp}{dx_1}$  and  $\frac{d^2 p}{dx_1^2}$ . After substitution of the general conditions  $\left(\frac{\partial^2 \xi_1}{\partial x_1^2}\right)_p = 0$  and  $\frac{d}{dx} \left(\frac{\partial^2 \xi_1}{\partial x_1^2}\right)_p = 0$  the expression for  $\frac{d^3 p}{dx_1^3}$  is reduced to:

$$\frac{d^3 p}{dx_1^3} = \frac{x_2 - x_1}{v_{21}} \frac{d^2}{dx^2} \left(\frac{\partial^2 \xi_1}{\partial x_1^2}\right)_p$$

and this expression is equal to 0, if  $x_1 = x_2$ , but not otherwise.

Without using the equations the same conclusions may be drawn geometrically from the properties of the saturation curve in the  $p-v$  diagram; if there are only one minimum and one maximum in the  $p-v_1$  curve, three points of intersection coincide in the critical point and consequently there is a point of inflexion, if on the other hand there is a minimum as well as two maxima, four points of intersection coincide in the critical point and there will be a maximum of the second order.

The whole argument thus turns on the question, whether it is legitimate to assume as self-evident, that the point, where  $x_1 = x_2$ , remains between the two points, where  $\left(\frac{\partial^2 \xi_1}{\partial x_1^2}\right)_p = 0$ ; that this is not the case follows from the fact that the condition  $x_1 = x_2$  is totally independent of the condition of critical contact between the two saturation curves: in fact there are cases, such as those referred to above, where the point  $x_1 = x_2$  lies at a far distance from the critical point, and others where there is no maximum or minimum at all, either outside or inside the three-phase triangle, such as for mixtures of ethane with the lower alcohol<sup>1)</sup>. The question therefore arises and has to be answered: how does the point where  $x_1 = x_2$ , which is known in many cases to be inside the two other maximum

<sup>1)</sup> KUENEN en ROBSON, Phil. Mag. (5) 48, p. 192, foll.

points at some distance from the critical temperature, appear outside in the realisable part of the diagram before the critical point is reached? The answer to this question is the following: the minimum ( $x_1 = x_2$ ) approaches one of the maxima ( $\left(\frac{\partial^2 \xi_1}{\partial x_1^2}\right)_p = 0$ ) and at a given temperature coincides with it; from the expressions for  $\frac{dp}{dx_1}$  and  $\frac{d^2p}{dx_1^2}$ , or by geometry, it follows that both coefficients vanish in this point and that the  $p-x_1$  curve has a point of inflexion with a tangent parallel to the  $x$ -axis. Immediately afterwards the two points in question have passed each other and have exchanged their character, i. e. the point, where  $\left(\frac{d^2 \xi_1}{dx_1^2}\right) = 0$ , is now a minimum<sup>2</sup>) and the other point, where  $x_1 = x_2$ , is a maximum: the latter point lies at first in the metastable part of the diagram between the minimum and one of the liquids of the three-phase equilibrium; a further change of temperature makes it coincide with this liquid and ultimately brings it outside into the stable part of the figure. The maximum and minimum in the non-stable part approach each other and finally coincide, as explained before.

For the sake of clearness we will once more go through the various changes as deduced above in the opposite order, i. e. while the temperature falls towards and passes through the critical point. Above the critical mixing-point there is a separate two-liquid curve turning its critical point towards the vapour-liquid curve: in the latter we assume a well defined maximum ( $x_1 = x_2$ ). When the temperature falls the two curves approach and at a given moment come into contact; this contact takes place in the critical point of the liquid curve, but in general at a smaller or larger distance from the maximum on the vapour-liquid curve: doubtless the distance may in some cases be small, but that does not affect the general argument; on further lowering of the temperature the maximum is in many cases taken up inside the three-phase equilibrium and so disappears from the realisable portion of the diagram; it passes successively the connodal and the spinodal curves and lies then ultimately in the non-stable region, where it is found at low temperatures.

It was mentioned in the beginning that similar changes occur in other cases, e.g. when the two-liquid curve lies inside the vapour-

<sup>2</sup>) Compare the figure for sulphurous acid and water, VAN DER WAALS, *Continuität II*, p. 18, fig. 3.

liquid curve at first and then appears outside, either on the temperature being raised, as is the case with mixtures of triethylamine and water<sup>1</sup>), or on lowering the temperature, as with propane and methylalcohol<sup>1</sup>); if in those cases a maximum vapour pressure exists, this maximum may disappear in a manner similar to the one sketched above.

The above conclusions may be summarised as follows:

The critical mixing-point of two liquids does not coincide with a point of maximum vapour pressure, if such a point exists; but the latter point may sooner or later at some distance from the critical point be enclosed inside the three-phase equilibrium; in the critical point the liquid branch of the saturation curve in the  $p-x$  diagram has a point of inflexion with a tangent parallel to the  $x$ -axis.

University College, *Dundee*.

**Physiology.** — “*Something concerning the growth of the lateral areas of the trunkdermatomata on the caudal portion of the upper extremity.*” By Prof. C. WINKLER from researches made in connection with Dr. G. VAN RIJNBEEK.

(Communicated in the meeting of November 28, 1903).

A methodical treatment of the dermatomata of the upper extremity offers very considerable difficulties, which have been confronted for the first time by the eminent labour of SHERRINGTON, though to our belief he has not wholly succeeded in conquering them.

The first difficulty we encounter, when essaying their physiological elaboration, is a technical one. The upper extremity transforms by its growth the dermatomata (of neck and trunk) situated above and beneath it. Owing to this transformation their extension-areas overlap one another mutually in a very peculiar manner, and only by means of cutting through numerous — sometimes from 7 to 9— adjacent posterior roots, it becomes possible to isolate them completely. The operation therefore presents greater difficulties, its duration is prolonged, its dangers are increased, partly because of the near vicinity of the medulla oblongata, partly because of the presence of the large perimedullar venous blood-reservoirs (air-embolus, hemorrhage).

The experimental definition of the extension of a root-area on the extremity, already more complicated than it is on the trunk, because

<sup>1</sup>) KUENEN, *Phil. Mag.* (6) 6, p. 637—653.

of the mutual removal of the neighbouring dermatomata, will be exposed moreover, in consequence of the more important operation, to a greater variability of shape, and we must be prepared to obtain only caricatures of its real shape.

In order however to undertake a just evaluation of these caricatures, it is necessary to know beforehand the variations in shape, suffered for the same reasons by the trunkdermatomata. A knowledge of the significance of the dorsal, lateral and ventral portions of the dermatoma, of their maxima and of their different reactions on a more or less serious trauma, is needed to enable us to understand the caricatures, obtained on the extremities. Even the technical mastership of SHERRINGTON has not wholly succeeded, we believe, in interpreting them truly.

The second difficulty, the perfect control of which we owe to SHERRINGTON, is found in the individual variations, presented by the animals experimented upon. On all dogs it is not always the same dermatomata that participate in the covering of the extremity. In most cases it will be the 5<sup>th</sup>—11<sup>th</sup> posterior roots that participate in the innervation of this extremity, yet it may sometimes occur that the 4<sup>th</sup>—10<sup>th</sup> (in cases of so-called pre-fixion), or also the 6<sup>th</sup>—12<sup>th</sup> (in cases of post-fixion) take their place. For this reason we cannot always be sure of the equivalence of two roots situated at the same height. The 9<sup>th</sup> root e.g. may (in cases of pre-fixion) take up the part generally performed by the 10<sup>th</sup>, or (in cases of post-fixion) that generally performed by the 8<sup>th</sup> etc.

Even if one is prepared by a previous knowledge of the trunkdermatomata for a true interpretation of the caricatures, and knows the dangers arising from pre- and post-fixion, it will still be necessary, as it has been done by SHERRINGTON, to describe the consequences of every separate isolation in the same manner, in order to retain one identical point of view for all of them.

In order to find this point of view, we have thought it convenient to adopt for the extremities mid-dorsal and mid-ventral lines, in the same way as had been done already by BOLK and SHERRINGTON; moreover we made use of a simple artifice.

As soon as a dermatoma has been isolated on an animal, employed for our experiments, and the boundaries of the insensible zones have been defined on the skin, the animal is photographed in different attitudes. When by these preliminaries we have obtained the photos necessary for controlling the experiment, the animal is killed, and the skin with the designs upon it, *after having been prepared further in a definite methodical manner*, is tanned and stretched, in order that it

may be compared with other similar skins, on which are designed likewise the boundaries of the isolated dermatomata.

This is done in the following manner. On the skin of the corpse the mid-ventral line of the trunk is drawn, and upon this line is designed on the sternum a point *C*, situated between the affixture of the 2<sup>d</sup> and 3<sup>d</sup> rib.

Beginning from this point, we next design, on the ventral side of the maximum abducted foreleg turned towards us, a line in the longitudinal axis, passing through the plica cubiti cranially of the epicondylus medialis humeri straight through the plant of the hand, towards the middle of the plant of the third finger.

This having been done on both sides, the stripping off of the skin may begin.

In the first place a circular incision, beginning above the third neck-vertebra is made around the neck, perpendicularly upon the longitudinal axis of the animal.

Next a similar circular incision is made around the trunk over the 17<sup>th</sup> vertebra.

Thirdly these two circular incisions are united by a skin-incision in the mid-ventral line.

Fourthly olecranon and epicondylus humeri medialis are marked on the skin by means of a striking colour.

Fifthly an incision is made on the extremity along the ventral line, continued through the plant of the third finger. That half of this latter situated next to the thumb, is stripped off, the web between the 3<sup>d</sup> and the 2<sup>d</sup> finger is split open between fore- and back-side; next the plant of the 2<sup>d</sup> finger is stripped off, the web between the 2<sup>d</sup> finger and the thumb is split, and the plant of the thumb is loosened.

The same operation is then performed for the finger-plants and webs of the ulnar fingers.

Finally the skin on the back-side of the fingers is loosened, the end-phalanges of each finger being cut one by one, in such a way, that the nails remain affixed to the skin of the back-side. Both hands being thus stripped off, the animal is flayed further.

The piece of skin, obtained in this manner, with the boundary-lines designed upon it, is next stretched, tanned and dried. Afterwards the insensible areas are coloured white by means of oil-paint and then varnished, and under control of the originally obtained photos such a piece of skin may be compared with other similar ones.

These skins are read in the following manner (fig. 1.5): *AA'* is the cranial boundary (the incision around the neck), *BB'* the caudal boundary (the incision around the trunk). Of course the point *C* recurs four

times on the boundary-line, as *C*, *C'*, *C''*, *C'''*. To the left and to the right *C''A* and *C'''A'* are the mid-ventral lines of the neck, *CB* and *C'B* those of the trunk. *COED* corresponds to the line drawn on the extremity, whilst the skin of the fingers, beginning to count from cranial to caudal part, is placed as follows: half of the plant of the 3<sup>d</sup> finger, the plant of the 2<sup>d</sup> finger, that of the thumb, the back-(nail)side of thumb, 2<sup>d</sup>, 3<sup>d</sup>, 4<sup>th</sup> and 5<sup>th</sup> finger, the plant of the 5<sup>th</sup> and 4<sup>th</sup> finger and the other half of the plant of the 3<sup>d</sup> finger. Two white spots indicate the position of the olecranon and that of the epicondylus humeri medialis.

*The 11<sup>th</sup> dermatoma.*

On October 3<sup>rd</sup> 1902, on a strong foxdog, designed as dog VI, by means of an incision in the skin to the left of the mid-dorsal line (in order to spare the dorsal nerve-branches of the neck to the right), the spinal column is discovered from the 4<sup>th</sup>—14<sup>th</sup> processus spinosus, and the arches of the 6<sup>th</sup>—14<sup>th</sup> vertebra are opened. Autopsy on October 8<sup>th</sup> confirms afterwards that to the right the 7<sup>th</sup>, 8<sup>th</sup>, 9<sup>th</sup>, 10<sup>th</sup>, 12<sup>th</sup>, 13<sup>th</sup> and 14<sup>th</sup> pair of spinal roots have been cut through, and that to the left the 11<sup>th</sup> root is cut through.

Reproductions on a reduced scale (fig. I) of the outlines of the photos and skin, represent the results of the determination of sensibility for maximum stimuli, performed on the 5<sup>th</sup>, 6<sup>th</sup> and 7<sup>th</sup> of October. On the right part of the body a sensible area is found, bounded cranially by an insensible zone, interrupted in its ventral, caudally by an insensible zone, interrupted in its lateral part (see fig. I, 1 and 2 and the right side of 5).

*a.* The dorsal portion of the cranial insensible zone is bounded cranially by a boundary-line, starting perpendicularly from the mid-dorsal line at the 7<sup>th</sup> vertebra, reaching after 10 c.m. the spina scapulae 3 c.m. below the acromion, then turning first in a cranial, afterwards again in a caudal direction, and continuing on the upper-arm towards the epicondylus humeri lateralis (the leg being stretched) (see fig. I, 1). Nearly 5 c.m. before reaching this latter, it takes a bend, slowly continuing in a caudal direction towards the epicondylus humeri medialis, which it does not reach either (see fig. I, 2). It then turns towards the mid-ventral line, approaching it to a distance of 6 c.m., enters profoundly into the axilla, and bends, continually deviating in a caudal direction, into the caudal boundary line of the insensible dorsal part. This caudal boundary line, directed towards the olecranon, parallel with the plica axillaris posterior (see fig. I, 2), forms an angle of 90° with itself before reaching the olecranon, continues in caudal direction, reaches the dorsal side of the upperarm, turns again rectangularly, and continues, with the exception of a caudally directed curve, straight unto the mid-dorsal line, which is reached at the 9<sup>th</sup> vertebra (see fig. I, 1 and 5).

*b.* The ventral part of the cranial insensible zone is found as a triangularly shaped area, commencing at the third rib, 5 c.m. below the manubrium sterni.

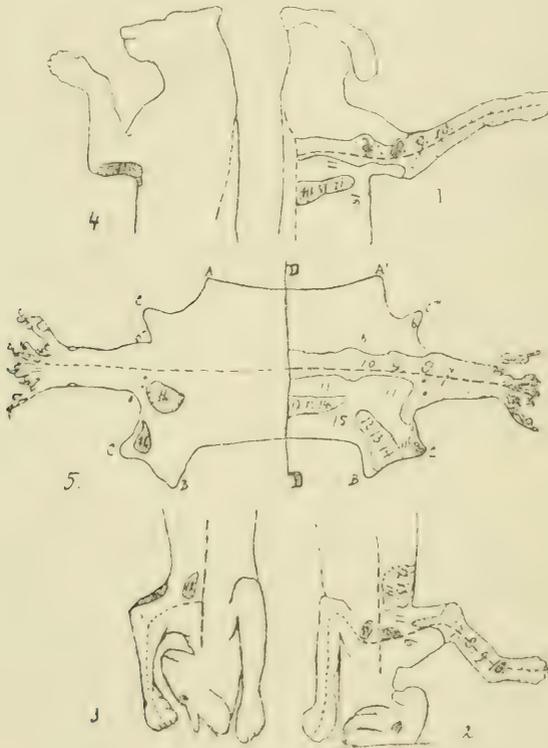
*c.* The dorsal part of the caudal insensible zone is shaped like a sugar-loaf (see fig. I, 1 and 5). The cranial boundary-line has its origin between

the 10<sup>th</sup> and 11<sup>th</sup> vertebrae, the caudal one at the 13<sup>th</sup> vertebra against the mid-dorsal line (fig. I, 1 and 5).

*d* The ventral part of the caudal zone is shaped like a rectangular triangle, having its hypotenuse along the plica axillaris posterior, and forming an outward curve in the direction of this latter (see fig. I, 2, 1 and 5).

*To the left* are found two insensible spots. One of these, opposite the sensible ventral portion to the right, is elliptic and advances obliquely towards the axilla (see fig. I, 2 and 3). The other, likewise elliptic, has its longitudinal axis almost perpendicular to that of the first, this latter being confluent with the plica axillaris posterior (see fig. I, 3, 4 and 5 to the left).

Fig. I. 11<sup>th</sup> root.



Dog VI. 11<sup>th</sup> root isolated to the right by cutting through the 7<sup>th</sup>, 8<sup>th</sup>, 9<sup>th</sup>, 10<sup>th</sup>, 12<sup>th</sup>, 13<sup>th</sup> and 14<sup>th</sup> roots, and cut through to the left.

*The 10<sup>th</sup> dermatoma.*

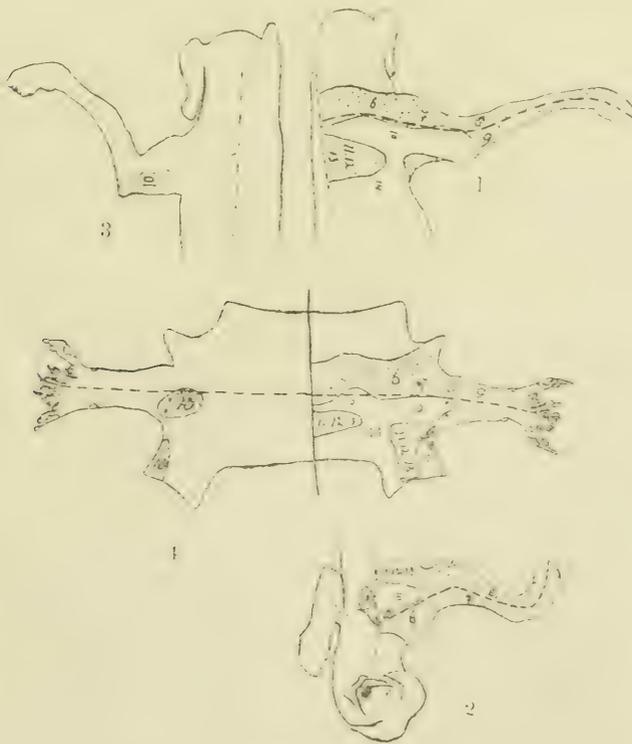
On September 19<sup>th</sup> 1902 on a strong male dog, designed as dog IV, by a similar operation as on dog VI, the 6<sup>th</sup>, 7<sup>th</sup>, 8<sup>th</sup>, 9<sup>th</sup>, 11<sup>th</sup>, 12<sup>th</sup> and 13<sup>th</sup> pair of roots *to the right* is cut through. *To the left* the 10<sup>th</sup> is cut through.

Autopsy on September 24<sup>th</sup> confirms this having been performed. A reproduction of the results found on Sept. 22<sup>th</sup> is given in fig. II.

To the right is found an *interrupted* sensible area, encompassed between two insensible zones.

a. The cranial insensible zone is bounded cranially by a line, leaving the mid-dorsal line at the 6<sup>th</sup> vertebra (see fig. II, 1), continuing in the direction of the acromion, and then, avoiding this and the caput humeri, taking a bend towards the mid-ventral line. It approaches this latter until a distance of 1½ cm. (see fig. II, 2), continues parallel to it for 4 cm. in a caudal direction, leaves it again at the third rib, borders cranially the sensible ventral triangle of the 10<sup>th</sup> dermatoma, thus becoming itself the caudal boundary line of the cranial insensible zone. As such it recedes to a distance of 8 cm. from the mid-ventral line, circumscribing next caudally the sensible triangle, it returns as the cranial boundary line of the caudal (interrupted) insensible zone to the mid-ventral line, approaching this to a distance of 1 c.m., taking again a caudal bend and accompanying it for 3 c.m. Next starting perpendicularly from the mid-ventral line, it continues along the plica axillaris posterior towards the upper-arm, in a cranial direction and turns with a sharp curve to the epicondylus medialis. Passing between olecranon and epicondylus, it circumscribes the first (see fig. II, 2 and 4), turns on the dorsal side of the arm towards the epicondylus lateralis, and

Fig. II. 10<sup>th</sup> root.



Dog IV. The 10<sup>th</sup> root isolated to the right by cutting through the 6<sup>th</sup>, 7<sup>th</sup>, 8<sup>th</sup>, 9<sup>th</sup>, 11<sup>th</sup>, 12<sup>th</sup> and 13<sup>th</sup> roots, cut through to the left.

returns, taking a rectangular bend, as the caudal boundary-line of the anterior insensible zone, after having made a caudal outward curve at the spina scapulae (3 c.m. from the acromion) to the mid-dorsal line between the 8<sup>th</sup> and 9<sup>th</sup> vertebra.

The caudal insensible zone is interrupted. The dorsal part forms a triangle, whose basis begins between the 9<sup>th</sup> and 10<sup>th</sup> vertebra and ends above the 13<sup>th</sup>, (see fig. II, 1).

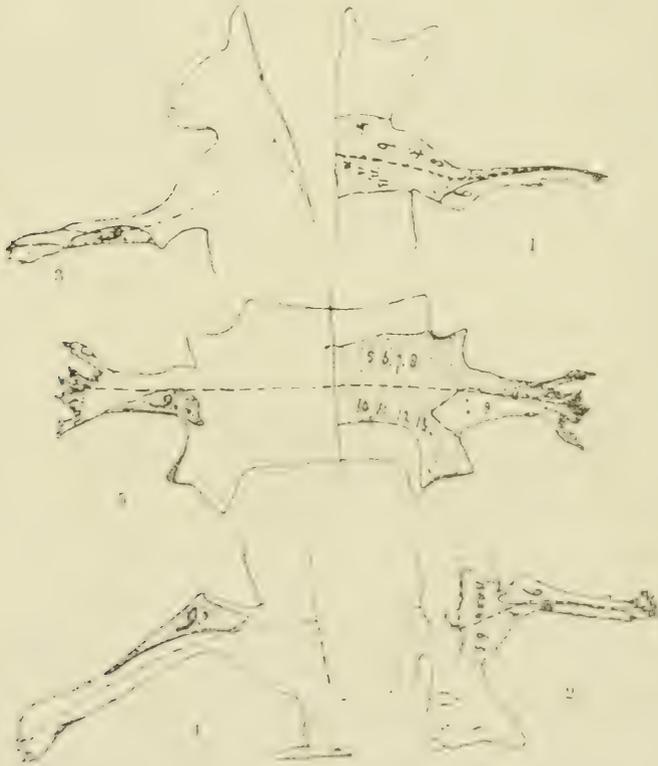
*To the left* are found two insensible spots. One of these, elliptic, opposite the sensible area at the mid-ventral line (see fig. II, 2 and 4). The other, likewise elliptic, having its longitudinal axis perpendicular to the mid-ventral line, and including olecranon and epicondylus humeri.

*The 9<sup>th</sup> dermatoma.*

On December 5<sup>th</sup> 1902, by a similar operation as before, on a strong grey foxdog, designed as dog IX, *to the right* the 5<sup>th</sup>, 6<sup>th</sup>, 7<sup>th</sup>, 8<sup>th</sup>, 10<sup>th</sup>, 11<sup>th</sup> and 12<sup>th</sup> pair of roots are cut through. *To the left* the 9<sup>th</sup> is cut through. Autopsy on Dec. 9<sup>th</sup> confirms this having been performed. On September 5<sup>th</sup> 1902 on a strong brown female dog, designed as dog I, *to the right* the 8<sup>th</sup> and 9<sup>th</sup> root, *to the left* the 9<sup>th</sup> root are cut through. Autopsy again confirms this.

Fig. III

9<sup>th</sup> root.



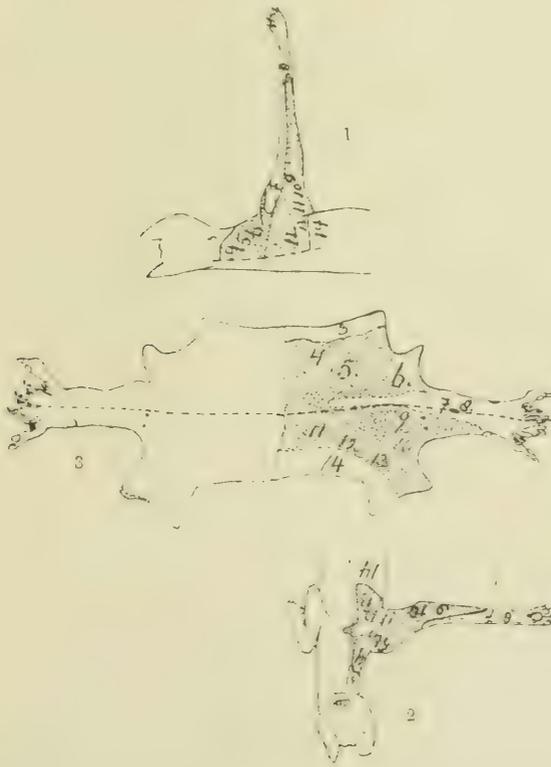
Dog IX. 9<sup>th</sup> root isolated to the right by cutting through the 5<sup>th</sup>, 6<sup>th</sup>, 7<sup>th</sup>, 8<sup>th</sup>, 10<sup>th</sup>, 11<sup>th</sup>, 12<sup>th</sup> and 13<sup>th</sup> root, cut through to the left.

A reduced reproduction of the photos and of the results of both experiments, in as much as they concern the 9<sup>th</sup> dermatoma, put together on one sheet, is given by fig. III (1, 2 and 5 to the right belonging to dog IX ; 3, 4 and 5 to the left belonging to dog I).

Dog IX : *To the right* the sensible area is encompassed by a large insensible zone, extending dorsally from the 4<sup>th</sup> to the 12<sup>th</sup> vertebra, ventrally from 5 c.m. below the manubrium sterni unto the middle of the neck. Its caudal boundary-line bends towards the mid ventral line in a forward convex arch, crossing first the scapular angle, and then following the plica axillaris posterior.

The description of the boundary-line of the sensible area may begin on the m. triceps (see fig. III, 2). From thence it bends on the ventral side of the extremity towards the sulcus bicipitalis medialis unto the commencement of the axilla, where it takes a turn in opposite direction, continuing caudally of the epicondylus medialis humeri, passing on the forearm over the thickest part of the flexores and reaching along the ulnar margin of the plant, the back of the hand between the 2<sup>d</sup> and 3<sup>d</sup> finger. Then it returns between the plant and the back of the fingers (the plant of the 3<sup>d</sup> and 4<sup>th</sup> finger having retained its sensibility, the back of both not), passing between the 4<sup>th</sup> and

Fig. IV. 7<sup>th</sup> and 8<sup>th</sup> root.



Dog VIII. The 7<sup>th</sup> and 8<sup>th</sup> root isolated to the right by cutting through the 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup>, 9<sup>th</sup>, 10<sup>th</sup>, 11<sup>th</sup>, 12<sup>th</sup> and 13<sup>th</sup>, to the left root 8 has been cut through.

5<sup>th</sup> finger on the back of the hand, and rising straight over the extensors of hand and fingers, between olecranon and epicondylus humeri lateralis, to the tricepstenon, which is crossed by it. On the foreside of the m. triceps it meets again its point of starting (see fig. III, 1).

Dog I: *to the left* are found two insensible spots. One of these is a very small one against the mid-ventral line at the affixion of the second rib.

The other, elliptic, having its longitudinal axis in that of the arm, is bounded by a line beginning high up in the axilla, continuing in the direction of the olecranon and avoiding this, passing on the dorsal surface of the extremity. It continues over the sinews of the extensors of hand and fingers until 1 c.m. before the plant, returns then on the ventral surface, crossing there the flexores, and passing beyond the plica cubiti cranially from the epicondylus humeri medialis, it takes a bend over the m. biceps. Crossing this muscle it reaches again, deviating in a caudal direction, its starting-point high up in the axilla.

*The 8<sup>th</sup> + the 7<sup>th</sup> dermatoma.*

On October 10<sup>th</sup> 1902 on a small black female dog, designed as dog VIII, are cut through *to the right* the 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup>, 9<sup>th</sup>, 10<sup>th</sup>, 11<sup>th</sup> and 12<sup>th</sup> pair of roots. *To the left* the 8<sup>th</sup> pair of roots is cut through. Autopsy on Oct. 13<sup>th</sup> verifies this. A reproduction of the result is found in fig. IV. *To the right* is a sensible area, encompassed by a large, continuous insensible zone, extending dorsally from the 3<sup>d</sup> to the 13<sup>th</sup> vertebra. Ventrally it extends from 5 c.m. above the manubrium unto 1 c.m. below it. Somewhere between the 2<sup>d</sup> and 3<sup>d</sup> rib its ventral boundary-line passes beyond the mid-ventral line *to the left*. The boundary-line of the sensible area begins at 1 c.m. caudally of the acromion, goes straight to the epicondylus humeri lateralis, and accompanies the ulna unto the fore-plant (see fig. IV, 1 and 3), then taking a sudden turn, it makes for the ventral surface of the extremity, that is reached halfway the fore-arm, crosses it obliquely through the elbow, regains the dorsal side on the upper-arm, and rejoins its starting-point below the acromion.

*To the left* no insensibility is found on the extremity, with the exception of a small insensible spot at the mid-ventral line of the trunk.

*The 9<sup>th</sup> + the 10<sup>th</sup> dermatoma.*

On Sept. 22<sup>th</sup> 1902 on a dark male dog, designed as dog V, are cut through, *to the right* the 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup>, 7<sup>th</sup>, 8<sup>th</sup>, 11<sup>th</sup>, 12<sup>th</sup>, 13<sup>th</sup> and 14<sup>th</sup> pair of roots. *To the left* the 10<sup>th</sup> is cut through.

Autopsy on Sept. 28<sup>th</sup> confirms this having been performed. A reproduction of the results is given by fig. V.

*To the right* two insensible zones encompass a sensible area. The cranial boundary-line of the cranial zone extends from the 3<sup>rd</sup> vertebra to the mid-ventral line 4 c.m. above the sternum. The caudal boundary-line of the caudal zone extends from the 13<sup>th</sup> vertebra to the mid-ventral line, nearly perpendicular to the longitudinal axis of the animal.

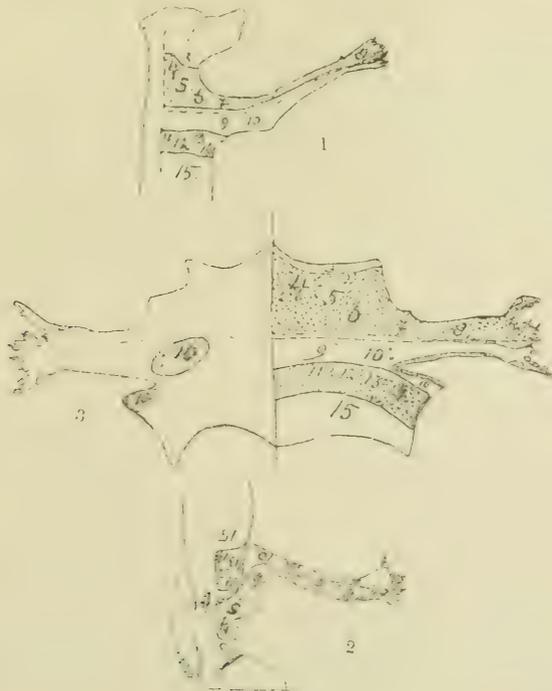
The cranial boundary-line of the sensible area starts from the mid-dorsal line at the 8<sup>th</sup> vertebra and continues straight towards the epicondylus

lateralis humeri, crossing the spina scapulae 3 c.m. below the acromion, following on the dorsal surface of the fore-arm the furrow between radius and ulna, and passing over the metacarpus of the little finger, between this and the 4<sup>th</sup> finger to the plant. Next it crosses the latter in a cranial direction, in such a manner that the plants of the fingers are insensible with the exception of the 4<sup>th</sup> and the 5<sup>th</sup>, circumscribes the plant of the hand and crosses again the hand towards the radial side, goes upward again, at first in the direction of the epicondylus humeri medialis, then taking a bend in the direction of the plica axillaris ventralis, approaching this very closely, and reaching the mid-ventral line, towards which it is directed perpendicularly, at the second rib.

The caudal boundary-line starts from the back at the 10<sup>th</sup> vertebra, continuing perpendicularly on the longitudinal axis, crosses the spina scapulae and continues parallel with the plica axillaris in a cranial direction until very close to the cranial border. Between the two a very narrow sensible area remains. It then takes a bend in caudal direction, reaching the mid-ventral line at the third rib.

To the left are two insensible spots. One of these is found opposite the 2<sup>nd</sup> and 3<sup>rd</sup> rib at the mid-ventral line. The other, elliptic, is almost identical with that found on dog IV.

Fig. V. 9<sup>th</sup> and 10<sup>th</sup> root.



Dog. V. 9<sup>th</sup> and 10<sup>th</sup> root isolated to the right by cutting through 4, 5, 6, 7, 8, 11, 12, 13 and 14, to the left 10 has been cut through.

*The 9<sup>th</sup> + the 6<sup>th</sup> dermatoma.*

On April 2<sup>nd</sup> 1902 on a dog, designed as dog XII the 4<sup>th</sup>, 5<sup>th</sup>, 7<sup>th</sup>, 8<sup>th</sup>, 10<sup>th</sup>, 11<sup>th</sup> and 12<sup>th</sup> pair of roots are cut through. Autopsy on April 8<sup>th</sup> confirms that such has been the case. A reproduction of the results is found in fig. VI.

To the right begins at the 3<sup>rd</sup> vertebra the cranial boundary-line of an insensible zone, at first perpendicular to the mid-dorsal line, then suddenly taking a bend in cranial direction (see fig. VI, 1 and 3), and approaching the mid-ventral line 4 c.m. above the manubrium. It then turns to continue parallel with the mid-ventral line until beyond the manubrium, rising next with a steep curve in the direction of the epicondylus humerus medialis, and bending back to reach again the sternum caudally of the second rib.

Fig. VI. 6<sup>th</sup> and 9<sup>th</sup> root.



Dog XII. 6<sup>th</sup> and 9<sup>th</sup> root isolated by cutting through 4, 5, 7, 8, 10, 11 and 12.

(The skin is here not quite in accordance with photo 2, the latter having been taken on April 5<sup>th</sup>. On April 7<sup>th</sup> a narrow sensible band had appeared, establishing a connection between the sensible ventral triangle and the sen-

sible zone on the extremity). The line then continues downward along the sternum until beyond the 4<sup>th</sup> rib, takes again a turn upward, and bending cranially it ends in a point near the extremity of the spina scapulae. Caudally there is found no insensible dorsal portion.

Near to the angulus scapulae, the line turns back again on the dorsal surface of the upper-arm, straight in the direction of the olecranon, 2 c.m. before reaching this, it takes a bend towards the ventral surface of the upper-arm, and crossing this, returns to the ventral portion. It is separated by a narrow zone from the sensible ventral triangle. (On the skin it passes here into the caudal boundary-line of the sensible ventral triangle). Above the latter it takes a turn in dorsal direction, and having reached again the dorsal surface on the middle of the upper-arm, it makes straight for the back, reaching this at the 6<sup>th</sup> vertebra.

Moreover there is found an insensible spot on the lower part of the extremity.

This has its beginning a little under the epicondylus humeri lateralis, it crosses longitudinally, the backside of the fore-arm likewise the hand and passes along the ulnar margin on to the plant, crosses along side the plants of the fingers which are insensible, and continues, taking a rectangular bend before the plant of the 4<sup>th</sup> finger, straight upward towards the epicondylus lateralis.

It is allowed to draw a few conclusions from these experiments.

1<sup>st</sup>. The caudal portions of those dermatomata, bounding the extremity caudally, especially of the 10<sup>th</sup> and the 11<sup>th</sup>, are pushed over the lower situated dermatomata.

We have observed already previously that, cranially of the 15<sup>th</sup> dermatoma, the cutting through of at least three adjoining roots is necessary, in order to obtain insensible dorsal spots. Only when 4 adjoining roots are cut through, a continuous insensible zone is found in that region. This presents a marked difference with the conditions existing on the trunk, where for the same purpose, the cutting through of two, resp. three roots, suffices.

This fact is confirmed here. By cutting through the 12<sup>th</sup>, 13<sup>th</sup> and 14<sup>th</sup> root (fig. I) or the 11<sup>th</sup>, 12<sup>th</sup> and 13<sup>th</sup> root (fig. II), analgetic areas are called into existence both dorsally and ventrally, but no continuous zones; when cutting through the 10<sup>th</sup>, 11<sup>th</sup> and 12<sup>th</sup> root (fig. VI), the analgetic dorsal area fails even, though the 10<sup>th</sup>, 11<sup>th</sup> and 12<sup>th</sup> dermatoma possess each of them a dorsal portion, which it is possible to isolate.

The significance of this fact is evident. The growth of the extremity in caudal direction, removes the caudal boundaries of the 10<sup>th</sup> and 11<sup>th</sup> dermatoma towards the caudal side. In the lateral part the 10<sup>th</sup> dermatoma overlaps the 14<sup>th</sup>, the 11<sup>th</sup> the 15<sup>th</sup>. The dorsal pieces of the 10<sup>th</sup>, 11<sup>th</sup> and 12<sup>th</sup> dermatoma are lying so near to one another or even covering one another, that the unimpaired 6<sup>th</sup>, 9<sup>th</sup> and 13<sup>th</sup> are able to provide together for the sensory innervation

along the back. The ventral pieces are pressed on one another against the sternum about the second rib.

2<sup>nd</sup>. The ventral and dorsal pieces, pressed on one another, are becoming gradually smaller and of less importance. It is only the lateral pieces that are pushing on the extremity.

In isolating the 11<sup>th</sup> dermatoma (fig. I. 5) it has been shown that the cranial portion of the lateral part of it is stretched on the extremity. At the same time its cranio-caudal axis is displaced. On the trunk it was parallel to that of the ventral and dorsal pieces, here it forms with them an acute resp. an obtuse angle. On the boundaries between lateral and ventral part the dermatoma suffers a rather deep indentation.

In isolating the 10<sup>th</sup> dermatoma (fig. II, 4) the stretching of the cranial lateral portion is even more important, and the difference in direction between the cranio-caudal axis of the lateral and that of the ventral part has become so great, that here they are already placed nearly perpendicularly to one another.

The indentation here has become so deep, that apparently the dermatoma has been split into two parts, the lateral piece being torn from the ventral. Apparently only, for most probably this result of isolating the 10<sup>th</sup> dermatoma is but a caricature. For in cases where it is isolated together with the 9<sup>th</sup> (fig. V) or with the 6<sup>th</sup> (fig. VI 3) dermatoma, a narrow sensible zone unites the ventral to the lateral area.

Thus much however is sure: only the lateral part, not the ventral part of the 10<sup>th</sup> dermatoma passes on the extremity.

Something similar happens for the dorsal pieces of the 10<sup>th</sup> and of the 11<sup>th</sup> dermatoma. Here we find likewise an indentation, though a less profound one, on the boundary of the lateral pieces towards their cranial side.

Yet there exists a great difference between the ventral and the dorsal indentations. Because of the fan-shaped extension of the displaced cranio-caudal axes of the lateral pieces, there must of necessity remain towards the ventral side, between two axes, close to the indentation, on the caudal portion of the extremity, a skin-area that owes its sensibility to one dermatoma only. Close to the dorsal indentation such is not the case.

This is shown if the 11<sup>th</sup> or 10<sup>th</sup> root are cut through. There are always produced two insensible areas, a small ventral area, such as we found much larger on the trunk and an area on the caudal portion of the extremity; where the lateral pieces of the 12<sup>th</sup> and 10<sup>th</sup> dermatoma no longer overlap the 11<sup>th</sup>, or those of the 11<sup>th</sup>

and 9<sup>th</sup> no longer the 10<sup>th</sup> dermatoma (see fig. I and II, left side).

After cutting through the 9<sup>th</sup> root (see fig. III to the left) we likewise may observe these two areas; by cutting through the 8<sup>th</sup> root no lateral insensible area is produced, at the utmost a very small one at the mid-ventral line.

The isolation of the 9<sup>th</sup> dermatoma (see fig. III to the right) shows, that the stretching has had a very strong effect on it. Neither ventrally nor dorsally it has retained any longer any connection with the mid-ventral and mid-dorsal lines, and only by projections shaped pointwise the direction of this lost connection is indicated.

But this does not prove that this sensible area is the whole of the dermatoma. Only its lateral portion is isolated there. Dorsal and ventral portion have dwindled away to insignificant pieces with a minimum sensory value, rapidly falling beneath the threshold. Isolation of the 9<sup>th</sup> dermatoma together with the 10<sup>th</sup> (see fig. V) produces however a very large dorsal area, and by cutting through the 9<sup>th</sup> root a very small ventral spot is still produced.

Much more probable than that it should pass as a whole on the extremity, it is therefore that the 9<sup>th</sup> dermatoma, like the 10<sup>th</sup>, sends only its lateral part on the caudal half of the extremity, whilst it still possesses a very small ventral spot (as may be shown by cutting through the root), perhaps even a still less important dorsal spot (that may be found by isolating the root together with one of the neighbouring ones, the 10<sup>th</sup> or the 6<sup>th</sup>).

But the 7<sup>th</sup> and eight dermatoma too, that have wholly lost the dorsal piece (see fig. IV to the right), send only their lateral pieces on the extremity. In cases where one ventral side has been made wholly insensible, if the 8<sup>th</sup> root on the other side is cut through, the consequence will even be a small outward curve passing beyond the mid-ventral line. But the 7<sup>th</sup> and the 8<sup>th</sup> dermatoma overlap one another completely. If the 8<sup>th</sup> root is cut through, there is found no lateral insensible area on the hand.

In short, the innervation of the extremity is provided for exclusively by the lateral parts of the dermatomata. Their ventral and dorsal parts become gradually smaller, and are at last (in as much as concerns the 7<sup>th</sup> and 8<sup>th</sup>) wholly or almost wholly lost.

Thus it has become possible to survey in a simple form the manner in which the extremity makes use of the lateral parts of the dermatoma.

A cone of the extremity growing in caudal direction, a lateral growth, meets on its way the lateral parts of the dermatomata (at

the very least 4) thickly pressed on one another, and pushes them forward in its course. It shoves before it the 7<sup>th</sup> and 8<sup>th</sup>, which remain situated on its top, overlapping one another for the greater part (c. f. fig. III and fig. VI). This however cannot be done without a considerable stretching, especially of the 9<sup>th</sup> and in a somewhat less degree of the 6<sup>th</sup>. Like the first floral leaves of an opening bud, on whose top are lying the 7<sup>th</sup> and 8<sup>th</sup>, the 9<sup>th</sup> dermatoma remains situated on the caudal, the 6<sup>th</sup> on the cranial side (see fig. VI) to the right. Caudally the 10<sup>th</sup> and cranially the 5<sup>th</sup> dermatoma are staying behind like the basal floral leaves of this bud.

The altogether different influence, exerted on the cranial dermatomata by the growth of the extremity in caudal direction, will be treated separately afterwards, but only the lateral portions pass on the extremity. Neither the conception of SHERRINGTON, representing the dermatomata passing as an unbroken whole on the extremity, nor that of BOLK, representing their latero-ventral parts (the 7<sup>th</sup> and 8<sup>th</sup> as a whole) moving roundabout an axis like the links of a chain, are capable of satisfying us completely, albeit our fundamental thoughts are the same, and borrowed from theirs.

Keeping provisorily to a mechanical conception, we regard the ranging of the dermatomata on the extremity as a consequence of the stretching of the lateral parts, caused by an impulsive force, beginning to act on the middle of the seventh and eighth dermatoma, and operating from centrum towards periphery in a caudal direction.

We hold it therefore not impossible that anatomy, in admitting or rejecting a homology between the skin-branches of the lateral intercostal nerves and those of the plexus brachialis, may either confirm or refute our conclusions.

**Chemistry.** — Professor FRANCHIMONT presents to the Library the dissertation of Dr. F. M. JAEGER on: "*Crystallographic and molecular symmetry of position isomeric benzene derivatives*" and gives a brief explanation of the same.

(Communicated in the meeting of November 28, 1903).

After MITSCHERLICH at the beginning of last century had discovered isomorphism and LAURENT some years later had pointed out certain form-analogies in the aromatic substitution-products, there appeared in 1870 the masterly researches of GROTH on morphotropy. From all this it might be surmised that, as all chemical and physical properties of organic compounds depend not only on their compo-

sition, but also on their chemical structure in the broadest sense this would also be the case with the crystalline form. Dr. JAEGER has, however, perceived that the relation between form and structure cannot be quite so simple and only stands a chance of being discovered by a very delicate investigation of properly chosen series of objects and he justifies the choice of the six isomeric tribromotoluenes used in his research: by their high molecular weight and the slight difference in chemical properties, so that practically, only the relative position of the groups of atoms in the molecule causes a difference and because the number of isomers is not too small.

Dr. JAEGER has prepared these substances, which were only known as fine needles, in a form suited to measurement and an accurate examination of them showed that four of them belong to the monoclinic, one to the rhombic and one to the tetragonal system. The last two are those with the vicinal position of the three bromine atoms. Of the first four there are two which exhibit an isomorphism bordering on identity and which can form mixed crystals in all proportions.

The densities of the four monoclinic forms do not differ greatly, that of the rhombic isomer, however, is smaller and that of the tetragonal form still smaller so that a higher symmetry of form is accompanied by a lesser density.

He further determined the fifteen possible melting point lines of the binary mixtures of the six isomers and obtained very notable results, some of which have already been mentioned by Dr. VAN LAAR at the last meeting.

From the isomorphism bordering on identity of the two monoclinic forms we may certainly conclude that there is great similarity in the structure of their chemical molecules although these are not expressed in our chemical formulae; they are the compounds 1. 2. 3. 5. and 1. 2. 4. 6. if  $\text{CH}_3$  stands on 1. This similarity appears, however, if we keep in view the analogy which exists, in a certain sense, between the group  $\text{CH}_3$  and a bromine atom, which has been noticed in a number of cases and which may be referred to a similarity in space relationships, volume perhaps. A conformity already pointed out by GROTH in 1870 and which has been since observed by many chemists, for instance in cases of so-called sterical obstacle.

The relations found by Dr. JAEGER between chemical and crystallographic symmetry have given rise to a number of problems, which he is now engaged in solving, for instance whether the isomorphism of the two monoclinic tribromotoluenes remains intact when substi-

tuting the other  $H$ -atoms by feeble morphotropic groups such as  $NO_2$ .

In regard to this, he recently informed me that both form a dinitroderivative, but with a different melting point and that not only the isomorphism is completely preserved, but that even the typical twin formation in certain solvents takes place with both in exactly the same manner, so that it looks as if one were dealing with the same material.

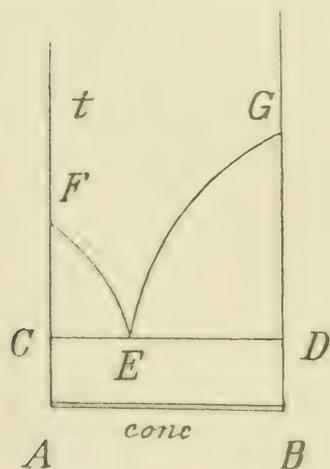
**Chemistry.** — “*The sublimation lines of binary mixtures*”. By Prof.

H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of November 28, 1903).

From the consideration of the  $p$ ,  $t$ ,  $x$ -representation of the equilibria for solid, liquid and gaseous phases of binary mixtures given by me a short time ago<sup>1)</sup> it may be deduced in what manner the evaporation of the mixtures of two *solid* substances, or inversely their condensation on cooling a mixture of vapours, takes place at a constant pressure by a change of temperature.

It is only necessary to take a  $t$ ,  $x$ -section at constant pressure through the figure at such a height, that no other equilibria occur than those between solid and vapour or between solid and solid. This is possible as long as we keep below the pressure of the quadruple-point where solid  $A$ , solid  $B$ , liquid and vapour coexist.



The adjoined figure then indicates the general character of the section, in which the vertical axis represents the temperature and the horizontal axis the concentrations of the mixtures.

$F$  is then the sublimation temperature of the pure substance  $A$ ,  $G$ , that of pure  $B$ . These temperatures are depressed along the lines  $F E$  and  $G E$  until, below the point  $E$ , total condensation of the vapour mixture to solid  $A +$  solid  $B$  occurs.

Conversely the sublimation commences at the temperature given by the line  $C E D$  and one of the two solid substances then disappears according to the concentration, unless the composition corresponds with  $E$ , in which case they both sublime simultaneously.

<sup>1)</sup> These Proc. V, p. 279.

If one of them has remained, the further sublimation takes place at a constantly increasing temperature until the point of the line  $FE$  or  $GE$  is reached, which corresponds with the original concentration of the mixture.

The whole figure is quite analogous with that representing the solidification or fusion of binary mixtures in which only the two components occur as solid phases,  $EF$  and  $GE$  resemble the melting point lines,  $E$  the eutectic point.

The analogy also holds good for the initial parts of the sublimation lines, for whose direction a formula similar to that for the lowering of the melting point may be deduced.

For the equilibrium of a single solid substance with its vapour we have the relation

$$\frac{dp}{dt} = \frac{Q}{2T^2}$$

which is true for the increase of the sublimation pressure, when  $Q$  represents the molecular heat of evaporation of the solid substance.

If we now assume that a small part of this line is straight and that  $Q$  is constant, then if the pressure  $p$  is diminished by  $\Delta p = 0.01 p$  the sublimation temperature will diminish by  $\Delta T$ , for which we find:

$$\Delta T \times \frac{Q}{2T^2} = \frac{\Delta p}{p} = 0.01$$

$$\Delta T = \frac{0.02 T^2}{Q}$$

If we now add to the vapour of the solid substance, which has at  $T - \Delta T$  a pressure  $p - 0.01 p$ , 1 mol. % of the vapour of a second substance, the total pressure again becomes  $p$  and  $T - \Delta T$  is therefore, at that pressure, the sublimation temperature of the solid substance with 1 mol. % of admixture. Consequently  $\Delta T$  is also the lowering of that sublimation temperature by 1 mol. % of admixture.

The formula for the decrease therefore corresponds perfectly with that for the molecular lowering of the freezing point, provided that we take for  $Q$  the molecular heat of sublimation.

The formula, however, only applies in the case of exceedingly small quantities of admixture, as the supposition that the  $p, t$ -line for the equilibrium of a single solid substance with its vapour is a straight one, is incorrect.

If we take into consideration its curvature, it follows that the sublimation lines of each solid substance of the mixture are concave to the  $x$ -axis.

The lower the sublimation temperature of the added substance, the further downward the course of the sublimation line of a solid substance will extend. If, therefore, gases are used as admixtures and in sufficient excess, any solid substance ought, theoretically, to volatilise at a very low temperature.

Of this circumstance advantage has often been taken in the artificial preparation of minerals by sublimation-methods in which gases or vapours ( $NH_4Cl$ ) have been used as second substance.

If, however, they exercise a chemical action on the others, the sublimation phenomena belong to systems of three or more components.

The sublimation phenomena may also be accompanied by phenomena of fusion, as may be deduced from an examination of other sections through my three dimensional figure.

**Chemistry.** — “*A quantitative research concerning BAEYER’s Tension Theory.*” By Prof. A. F. HOLLEMAN and Dr. G. L. VOERMAN.

(Communicated in the meeting of November 28, 1903).

BAEYER’s tension theory gives an explanation of numerous phenomena in organic chemistry, but it is, however, almost exclusively of a qualitative nature. The preference for the formation of cyclic compounds with 5 and the instability of cycle systems with a larger or smaller number of atoms required by the theory are confirmed in many instances. Meanwhile as far as I am aware, that “preference” and that “instability” has never been expressed in figures. And so long as this is not the case such expressions remain vague, as we do not possess any measure with which we can gauge the “preference” for the cycle formation with 5 over one with a different number of atoms, and also are not in a position to compare the stability of one compound with that of another.

I, therefore, suggested to Dr. VOERMAN to investigate quantitatively the relative stability of the members of a special class of cyclic systems, namely the anhydrides of the dibasic acids of the normal saturated series. They are again converted by the action of water into the dibasic acids. The ease with which they re-absorb water must depend on the degree of tension in the ring contained in these anhydrides, as the ring opens and the bonds then can retake their normal position. The velocity with which these anhydrides are converted into the corresponding acids may therefore, be taken as the measure of the tension in the ring.

Dr. VOERMAN has first of all prepared these anhydrides, then dissolved them in a large amount of water and determined the velocity of their transformation into acids.

The anhydrides investigated were those of succinic acid ( $C_4$ ), glutaric acid ( $C_5$ ), adipinic acid ( $C_6$ ), pimelic acid ( $C_7$ ), suberic acid ( $C_8$ ), azelaic acid ( $C_9$ ) and sebacic acid ( $C_{10}$ ). Many of these acids are difficult to procure, but Dr. VOERMAN has succeeded in greatly improving their mode of preparation, for the particulars of which we refer to a communication shortly to appear in the *Recueil*.

In order to determine the velocity with which these anhydrides pass into acids when introduced into water, it was necessary to be able to determine at any given moment the quantity of acid which had already been formed. This is done by measuring the electric conductivity of the solution, taking it for granted that the solution of the anhydride does not conduct the current.

This supposition is first of all justified by the observation that the conductive power of the anhydride solution is smaller the sooner it is measured after it has been prepared and secondly because the acid anhydrides do not belong to the class of electrolytes. In order to obtain the concentration of the acid in the solution from its conductivity it is only necessary to measure the conductivities of solutions of the acids at the temperature employed over the range of concentrations which is considered in the experiments. These measurements were conducted by Dr. VOERMAN, who generally used the acids which were recovered from the anhydrides by the action of water in order to work under quite the same conditions as existed in his velocity determinations. As might, however, have been expected the same values were obtained for the conductivity of the acids themselves and those recovered from their anhydrides.

As the concentration of the acid, after the complete conversion of the anhydride, in the velocity measurements did not exceed  $\frac{1}{2}$  normal, the quantity of water may be taken as constant, so that the conversion may be represented by the equation for unimolecular reactions. This indeed, gave satisfactory values for the constant occurring therein.

It is, however, only in the case of the anhydrides of succinic and glutaric acids that Dr. VOERMAN has obtained satisfactory determinations, at  $25^\circ$ , of the values of  $K = \frac{1}{t_2 - t_1} \log \frac{C_1}{C_2}$  ( $t$  in minutes,  $C =$  gm. mol. per Litre).

He obtained the values 0.1683, and 0.1708 showing that the 5-ring is somewhat more stable than the 6-ring. In the case of the

higher anhydrides we met with an obstacle which prevented accurate measurements. This was their small solubility in water. He always noticed in their solutions a gradual increase in the electric conductive power showing that they first dissolve as such before being converted into acids, but this increase was too small to allow the velocity constant to be calculated. It is worthy of note that although when boiled with water they form only globules which are but slowly converted into acids, they are so hygroscopic that they keep but a short time unchanged when exposed to the air. This may, perhaps be attributed to the fact that water in the liquid condition consists mainly of polymeric molecules, whereas in the state of vapour they are normal. The anhydrides of glutaric and succinic acid do not show this peculiarity.

But the higher anhydrides also differ in another respect from the two first mentioned namely in their molecular complexity. Determinations of the boiling points of their solutions in acetone show that they are much polymerised whilst the anhydrides of succinic and glutaric acids behave normally. This, perhaps, explains their difficult solubility in water.

*Groningen, Lab. Univers. Nov. '03.*

**Astronomy.** — *“Investigation of the errors of the tables of the moon of HANSEN—NEWCOMB in the years 1895—1902.”* By Dr. E. F. VAN DE SANDE BAKHUYZEN. (2<sup>nd</sup> Paper).

(Communicated in the meeting of September 26 1903).

14. After my previous paper under this title was read at the meeting of the Academy of June 27, 1903, a preliminary communication on the investigation undertaken at Greenwich on similar lines has also been published. Mr. P. H. COWELL who was occupied with this work gave a summary of his results in *“The Observatory”* of September 1903 in a paper under the title *“Analysis of the errors of the moon”*, which he kindly sent to me in advance of publication.

Mr. COWELL utilized for his investigation the observations of right ascension of the period 1883—1898. His method in the main agrees with that used by NEWCOMB in his *“Investigation”*, which I had also followed and our results for the years 1895—98 are substantially in accordance. In the second place he compared his empirical results with those derived from theory.

This last part of COWELL's paper has drawn my attention to the

fact that the theoretical formulæ which I had used for the same comparison were incomplete. For I had not noticed that RADAU in his valuable "*Recherches concernant les inégalités planétaires du mouvement de la lune*"<sup>1)</sup>, had found that besides the "Jovian Evection" there exist some other inequalities of a nearly monthly period with appreciable coefficients. Nor had I paid attention to the fact that according to HILL's researches on the inequalities resulting from the figure of the earth<sup>2)</sup>, made following DELAUNAY's method, an appreciable term of monthly period must be added to those inserted into the tables of HANSEN.

It is this gap of my preceding investigation which I shall here try to fill up. But I shall go no farther, for from the beginning the aim of my work was limited and there would be still less reason to continue it, now that Mr. COWELL intends to continue his work and to extend it also to other periods.

15. The principal terms of a nearly monthly period which, according to RADAU and HILL, are still to be added to the true longitude from HANSEN's tables are:

$$- 0''.68 \sin (g + 2 \pi + 3 V - 5 E) \dots \dots \dots (I)$$

$$- 0.88 \sin (g + 2 \pi - 2 J) \dots \dots \dots (II)$$

$$+ 0.32 \sin (g + 2 \pi - 3 J + 7^\circ) \dots \dots \dots (III)$$

$$+ 0.45 \sin \theta \cos g \dots \dots \dots (IV)$$

where  $V$ ,  $E$  and  $J$  represent the mean longitude of Venus, the Earth and Jupiter. The first three are terms found by RADAU as arising from the planets, while the fourth expresses the difference between the inequalities arising from the figure of the earth after HILL and after HANSEN<sup>3)</sup>.

<sup>1)</sup> *Annales de l'Observatoire de Paris. Mémoires* T. XXI.

<sup>2)</sup> G. W. HILL Determination of the inequalities of the moon's motion which are produced by the figure of the earth. *Astron. papers American Ephemeris and Naut. Alm.* Vol III. Part. II.

<sup>3)</sup> Comp. also COWELL l.c. COWELL introduces still two other terms, numbered by him 2 and 6 (Observ. p. 350). It seems doubtful to me whether their introduction is sufficiently justified.

As to 2, we must, if we consider NEWCOMB's empirical term of long period as an inequality of the mean longitude, like the first Venus-inequality of HANSEN, and this seems the most plausible, also accept the inequality of short period in the true longitude connected with it.

COWELL's correction 6 results from the rejection of HANSEN's constant term in the latitude  $- 1''.00$ . It seems however that the correction of the tabular latitude or declination with  $+ 1''.00$  is *a posteriori* not justified. From a comparison of the declinations determined at Greenwich in the years 1895—1902 I found as the mean difference Obs.—Comp.  $- 0''.17$ , and after the reduction to NEWCOMB's

The second term — the Jovian evection, whose coefficient given here according to RADAU agrees almost exactly with HILL's value — and the 4<sup>th</sup> term give rise in the coefficients of  $\sin g$  and  $\cos g$  to terms of a period of about 18 years (the exact periods are 17.41 and 18.61 years respectively), while the periods of  $2\pi + 3V - 5E$  and of  $2\pi - 3J + 7^\circ$  amount to 9.74 and 37.25 years respectively, i. e. about half and double the length of the former.

The combined influence of the theoretical terms II and IV therefore must be represented approximately by NEWCOMB's and my empirical term, for which I found a period of 18.6 years, and the other terms can have but little influence on its determination. In one respect, however, the method followed in our computations will be erroneous: we have wrongly assumed that  $h'$  and  $k'$  have the same argument as well as the same coefficient.

To investigate in how far the different theoretical terms were confirmed by the observations I have proceeded as follows. On the one hand I have tried to find whether the formulae determined originally for  $h$  and  $k$ , where the equality of argument and coefficient was not yet assumed, point to the existence of the term IV. On the other hand I have investigated whether the differences found before between the observed and the computed  $h$  and  $k$  point to the existence of the terms I and III. For their influence must be exhibited in those differences.

If we take 1876.0 as zero epoch and assume for the annual variation of the argument the value finally found  $+19^\circ.35$ , the first formulae derived on p. 379 of my first paper are.

$$h = +0''.45 - 1''.30 \sin [317^\circ.1 + 19^\circ.35 (t - 1876.0)]$$

$$k = +0''.26 + 1''.46 \cos [299^\circ.3 + 19^\circ.35 (t - 1876.0)]$$

If we assume that the variable part of  $k$  must consist in: 1<sup>st</sup>. a term which agrees in argument and coefficient with the variable part of  $h$ , and 2<sup>nd</sup>. a term of the form IV, we find for the latter:

Fundamental Catalogue this becomes  $+0''.13$ . NEWCOMB found (*Invest.* p. 33) for 1862—73 as mean difference: Declination observed at Greenwich — Tabular Declination  $+0''.36$ . Constant corrections had already been applied to the observations by NEWCOMB and, if accounting for them I now reduce the results to NEWCOMB's F. C., I find Obs.—Comp. =  $-0''.08$ . So the constant correction to be applied to the tabular declinations is found to be small for the two periods. (Comp. also below section 18 last part).

If the observations were reduced with NEWCOMB's value of the moon's parallax, the differences Obs.—Comp. would be about  $+0''.44$  and  $+0''.23$  (*last part added* 1903 Dec.)

$$\begin{aligned}
 k_{IV} &= + 1''.46 \cos [299^\circ.3 + 19^\circ.35 (t - 1876.0)] \\
 &\quad - 1''.30 \cos [317^\circ.1 + 19^\circ.35 (t - 1876.0)] \\
 &= + 0''.46 \sin [328^\circ + 19^\circ.35 (t - 1876.0)]
 \end{aligned}$$

while, according to theory, this ought to be:

$$k_{IV} = + 0''.45 \sin [357^\circ + 19^\circ.35 (t - 1876.0)]$$

which, considering the great uncertainty in the difference between the two empirical terms, is a satisfactory agreement<sup>1)</sup>.

In the second place we shall try to find whether the differences between the observed  $h$  and  $k$  and those derived from the formulæ in the 1<sup>st</sup> paper, p. 382 reveal the influence of the terms I and III. Therefore I shall give here those differences, which formerly were omitted. They are found in the following table (p. 416) under the headings Obs.—Comp. I. The contents of the columns Obs.—Comp. II will be explained later.

The differences Obs.—Comp. I will serve in the first place to find what the observations teach us about the term I. I have therefore arranged them according to the values of the argument  $2\pi + 3V - 5E$ , and by mutually combining the results of the 3 series, of which the means had first been reduced to zero, with the weights 1, 3 and 2, we obtained the following 10 normal values for  $\Delta h$  and  $\Delta k$ .

Arg.	$\Delta h$	$\Delta k$
319°	-0''15	+0''11
356	-0.34	+0.08
33	+0.29	-0.29
70	+0.83	-0.18
107	+0.08	+0.32
143	-0.21	+0.11
180	+0.04	-0.18
217	-0.02	+0.03
254	-0.28	+0.10
291	-0.44	-0.15

<sup>1)</sup> The results of p. 382 of the first paper would seem to point to a greater difference between the coefficients of the variable parts of  $h$  and  $k$ ; this would improve the agreement between the empirical and the theoretical argument of  $k_{IV}$ .

	$\Delta h$		$\Delta k$	
	<i>O-C I</i>	<i>O-C II</i>	<i>O-C I</i>	<i>O-C II</i>
1847.8	+0 <sup>o</sup> 91	+0 <sup>o</sup> 48	+0 <sup>o</sup> 97	+1 <sup>o</sup> 28
1848.9	+0.41	-0.24	--0.55	-0.43
1850.1	-0.03	-0.29	-0.78	-0.25
1851.2	-0.71	-0.83	-0.71	-0.13
1852.4	-0.69	-0.68	-1.38	-0.78
1853.5	-0.27	-0.45	-1.43	-0.54
1854.6	-0.20	+0.03	-1.40	-0.56
1855.8	-0.99	-0.66	+0.02	+0.43
1856.9	+0.41	+0.49	+1.01	+1.29
1858.1	-1.49	-1.11	-0.62	-0.52
1862.5	+0.68	+0.79	-0.10	-0.47
1863.5	+0.32	+0.33	+0.83	+0.45
1864.5	+0.05	-0.03	+0.60	+0.22
1865.5	+0.09	-0.07	-0.17	-0.52
1866.5	+0.49	+0.29	+0.57	+0.27
1867.5	-0.27	-0.52	+0.47	+0.26
1868.5	+0.60	+0.33	-0.37	-0.49
1869.5	+1.44	+1.16	-0.35	-0.41
1870.5	+0.77	+0.50	+0.01	+0.01
1871.5	+0.51	+0.26	+0.59	+0.64
1872.5	+0.65	+0.42	+0.47	+0.56
1873.5	+0.21	-0.01	+0.32	+0.41
1874.5	+0.46	-0.05	+0.28	+0.35
1895.5	-0.96	-0.55	-0.91	-0.84
1896.5	-0.17	+0.19	-0.43	-0.49
1897.5	+0.21	+0.51	+0.08	-0.09
1898.5	+0.64	+0.88	+0.48	+0.21
1899.5	-0.37	-0.22	+1.43	+1.10
1900.5	-0.77	-0.73	+0.07	-0.28
1901.5	-0.36	-0.41	-0.07	-0.44
1902.5	-0.05	-0.19	-0.10	-0.45

Hence, by solving the 10 equations by least squares, we derive:

$$\angle h = + 0''.92 \cos (2 \pi + 3 J - 5 E)$$

$$\angle k = - 0''.00 \sin (2 \pi + 3 J - 5 E)$$

while according to theory the two coefficients ought to be  $+ 0''.68$ .

Thus it seems that the term I is not confirmed by the observations used here. I shall show later that a somewhat modified computation leads to the same result. It may be that in the years considered here another inequality has neutralized its effect.

In the second place we shall try to find what may be derived from the O.—C. I about the term III. I have therefore arranged the  $\angle h$  and  $\angle k$  according to the values of  $2 \pi - 3 J + 7^\circ$  and found the following normal values which, however, do not cover a full revolution of the argument.

Arg.	$\Delta h$	$\Delta k$
225°	+0''.34	+0''.36
255	+0.82	-0.03
285	+0.10	+0.29
315	-0.02	+0.20
345	+0.16	+0.67
15	-0.63	-0.24
45	-0.48	-0.74
75	-0.48	-0.96
105	+0.51	+0.21

I have represented these values by the expressions:

$$\angle h = a + b \cos (2 \pi - 3 J + 7^\circ)$$

$$\angle k = a' + b' \sin (2 \pi - 3 J + 7^\circ)$$

and by solving the equations by least squares I found:

$$b = - 0''.55$$

$$b' = - 0''.40$$

or from the  $\angle h$  and  $\angle k$  combined:

$$b = b' = - 0''.46$$

while the theoretical value is  $- 0''.32$ .

The empirical determination of these coefficients is still very uncertain. In so far as the observations have a conclusive force, we may say that they confirm the inequality III.

The final result of the foregoing investigation is therefore that the observations confirm the existence of the inequalities III and IV, but that they seem to contradict the existence of the term I.

16. I then made a new determination of the principal term of the empirical inequality, after first having corrected the  $h$  and  $k$  for the inequalities III and IV, for which I accepted the theoretical values.

From the  $h$  and  $k$  for each year corrected thus, from which moreover the constants  $h_c = +0''.55$  and  $k_c = +0''.26$  were subtracted<sup>1)</sup>, I have first derived the values of  $N$ . They follow here:

	$N$	$O-C$		$N$	$O-C$
1847.8	55°	-66°	1868.5	173°	+12°
1848.9	137	- 5	1869.5	211	+30
1850.1	155	-10	1870.5	213	+13
1851.2	152	- 35	1871.5	245	+26
1852.4	175	-35	1872.5	262	+23
1853.5	207	-24	1873.5	273	+15
1854.6	227	-25	1874.5	290	+13
1855.8	314	+38	1895.5	333	+ 8
1856.9	320	+23	1896.5	327	-17
1858.1	47	+87	1897.5	343	-20
1862.5	35	-10	1898.5	349	- 34
1863.5	47	-18	1899.5	31	-11
1864.5	80	- 4	1900.5	83	+22
1865.5	122	+19	1901.5	100	+19
1866.5	119	- 4	1902.5	116	+16
1867.5	120	-22			

If to these values we assign the same weights as before, we obtain the following normal values:

<sup>1)</sup> These values of the constants were found as a first approximation after the inequality III had been accounted for. The differences between them and those which were finally found,  $+0''.43$  and  $+0''.17$  are unimportant in comparison with the great systematic discordances which still remain.

1852.6	$N = 200.3$	Weight 1	$O - C = - 13^{\circ}.7$
1868.5	168.7	3	+ 7 .0
1898.5	18.9	2	- 3 .6

whence

$$N = 306^{\circ}.9 + 19^{\circ}.36 (t - 1876.0)$$

The annual variation of  $N$  according to the new formula is practically equal to the value found before. The values of  $O - C$  which are joined to those of  $N$  in the table above show, however, that the systematic discordances are still great and the outstanding errors of the three normal values are even somewhat greater than before.

In the second place I have determined anew the coefficient of the inequality. I have not done this by deriving directly values for each year from the corrected  $h$  and  $k$  and then taking the mean of the separate values, as by doing so I should have obtained a too large coefficient. But I have represented the corrected  $h$  and  $k$  by the formulae:

$$\begin{aligned} h' &= - a \sin N \\ k' &= + a \cos N \end{aligned}$$

assuming for  $N$  the computed values.

In this way I derived

$$\begin{aligned} \text{from the } h' & \quad a = + 1''.23 \\ \text{from the } k' & \quad = + 1 .34 \\ \text{from the two combined} & \quad a = + 1 .28. \end{aligned}$$

Hence the formulae for  $h'$  and  $k'$  become

$$\begin{aligned} h' &= - 1''.28 \sin [307^{\circ} + 19^{\circ}.4 (t - 1876.0)] \\ k' &= + 1''.28 \cos [307^{\circ} + 19^{\circ}.4 (t - 1876.0)] \end{aligned}$$

while from the theoretical term II, the Jovian Evection, there would follow:

$$\begin{aligned} h_{II} &= - 0''.88 \sin [329^{\circ} + 20^{\circ}.68 (t - 1876.0)] \\ k_{II} &= + 0''.88 \cos [329^{\circ} + 20^{\circ}.68 (t - 1876.0)]. \end{aligned}$$

There still remains a considerable difference between the empirical and the theoretical values; for 1902 the difference between the arguments amounts to as much as  $57^{\circ}$ . Therefore we cannot but conclude that still other inequalities join their influence to that of the Jovian Evection.

17. The expressions obtained for  $h$  and  $k$  according to the two preceding sections are therefore:

$$\begin{aligned} h &= h_c + h' + h_{III} \\ k &= k_c + k' + k_{III} + k_{IV} \end{aligned}$$

For  $h_c$  and  $k_c$  we find from the mean of all the observations used here :

$$\begin{aligned} h_c &= + 0''.43 \\ k_c &= \cdot 0''.17 \end{aligned}$$

so that the complete formulæ become :

$$\begin{aligned} h &= + 0''.43 - 1''.28 \sin [307^\circ + 19^\circ.4(t-1876.0)] - 0''.32 \cos (2\pi - 3J + 7^\circ) \\ k &= + 0''.17 + 1''.28 \cos [307^\circ + 19^\circ.4(t-1876.0)] - 0''.32 \sin (2\pi - 3J + 7^\circ) \\ &\quad - 0''.45 \sin \theta \end{aligned}$$

or putting for  $2\pi - 3J + 7^\circ$  and for  $\theta$  their values and combining the terms  $h'$  and  $k_{IV}$  which have the same period :

$$\begin{aligned} h &= + 0''.43 - 1''.28 \sin [307^\circ + 19^\circ.4(t-1876.0)] \\ &\quad - 0''.32 \cos [198^\circ - 9^\circ.67(t-1876.0)] \\ k &= + 0''.17 + 1''.65 \cos [297^\circ + 19^\circ.4(t-1876.0)] \\ &\quad - 0''.32 \sin [198^\circ - 9^\circ.67(t-1876.0)] \end{aligned}$$

The values derived from these formulæ I call Comp. II and the differences between these and the  $h$  and  $k$  derived directly from the observations are shown in the table of page 416 under the headings  $O-C'II$ .

Also the  $O-C'II$  still show a distinct systematic character. The number of permanencies of sign has but little diminished, yet the mean discordance has become somewhat smaller.

We find :

Mean discordance from C. I	in $h \pm 0''.62$	in $k \pm 0''.68$
.. .. from C. II	in $h \pm 0''.53$	in $k \pm 0''.57$

while using only the second and third series we should have found :

Mean discordance from C. I	in $h \pm 0''.57$	in $k \pm 0''.54$
.. .. from C. II	in $h \pm 0''.50$	in $k \pm 0''.49$

Finally I have employed the differences  $O-C'II$  to investigate once more whether the observations reveal an inequality with a period of 9.74 years. Disregarding the less accurate first series, and using directly the annual results, I found :

$$\begin{aligned} \text{for the term in } h &+ 0''.04 \cos (2\pi + 3V - 5E) \\ \text{for the term in } k &+ 0''.08 \sin (2\pi + 3V - 5E) \end{aligned}$$

As we see the coefficients are again found to be small, while their theoretical value amounts to  $+ 0''.68$ .

18. After the communication of my first paper to the Academy, I have still made some new calculations about the errors of latitude, of which the results follow here.

The computation given on p. 386 of my first paper had shown that especially the values of  $b$  from the equation

$$\Delta\delta = a + b \sin u + c \cos u$$

as derived separately from the years 1895—98, and from 1899—1902 were not in good agreement, and that between the  $\Delta\delta$  for the same value of  $u$  from both periods there exist distinct systematic differences.

Therefore I have also solved rigorously the equations for the separate years. As the  $\Delta\delta$  for the period investigated by NEWCOMB are less accurate (therefore NEWCOMB himself used only the mean values for the whole period) I have solved for this period not the equations for the separate years but those for groups of 2 or 3 years.

In this way I obtained the following values of  $a$ ,  $b$  and  $c$ . To the  $c$  of 1895—1902 the corrections mentioned before have been applied. The values of  $a$  derived from the two series are not directly comparable inter se, as the declinations were not reduced to the same system <sup>1)</sup>.

	$a$	$b$	$c$
1862—64	-0''16	+0''62	+0''61
1865—66	+0.27	+0.27	+0.57
1867—68	-0.38	+0.02	+0.25
1869—70	-0.38	+0.50	+0.60
1871—72	-0.14	-0.13	-0.08
1873—74	-0.32	-0.65	+0.39
1895	+0.16	-0.76	+0.81
1896	-0.29	0.17	+1.12
1897	-0.27	-0.07	+1.11
1898	+0.08	+0.15	+1.89
1899	+0.35	+0.79	+1.02
1900	+0.55	+0.45	+0.89
1901	+0.51	+0.50	+0.40
1902	+0.43	+0.78	+0.79

To these results we may add those for 1892 derived by FRANZ. I had at first overlooked the fact that FRANZ had not only discussed his own observations of the crater Mösting A, but also the results of a similar series of observations made in the same years at

<sup>1)</sup> Comp. also the remark at the end of this section.

Göttingen<sup>1)</sup>. As the most probable results from the two series he found:<sup>2)</sup>

$$\begin{aligned} di &= + 0'.46 \\ id\theta &= + 0''.77 \\ d\theta &= + 8''.7 \end{aligned}$$

These values correspond to

$$b = - 0''.44 \quad c = + 0''.74.$$

Considering these results it seems possible that we must assume the existence of a periodic term in  $b$ . But for the present we cannot go farther and we must await the results of other series of observations before we can formulate more definite conclusions.

I will now only add the following remark. As within each year the observations are fairly regularly distributed over the anomalistic revolution, the fact that in the present investigation we have disregarded the corrections of the longitude depending on  $g$  cannot have had an appreciable influence on the determination of the  $b$  and  $c$  from the separate years. On the other hand an apparent periodicity in the  $a$  may have arisen from it.

The corrections of the longitude alluded to are of the form:

$$\delta l = s \sin (g + \chi)$$

where  $\chi$  is a slowly varying angle. The corresponding corrections that ought to be applied to the declinations are:

$$\begin{aligned} \delta \delta &= 0.40 \cos l \times s \sin (g + \chi) \\ &= 0.20 s \sin (2g + \pi + \chi) - 0.20 s \sin (\pi - \chi) \end{aligned}$$

i. e. partly nearly half-monthly terms, partly terms of long period which modify the values found for  $a$ .

From the largest term in the correction of the longitude:

$$\delta l = + 1''.28 \sin (g + N - 90^\circ)$$

arises a term:

$$\delta \delta = - 0''.26 \sin (\pi - N + 90^\circ)$$

which term has a period of 17 years.

**Astronomy.** — *“Investigation of the errors of the tables of the moon of HANSEN—NEWCOMB in the years 1895—1902.”* By Dr. E. F. VAN DE SANDE BAKHUIZEN. (Second paper, part II). (Communicated in the meeting of November 28, 1903.)

19. In the preceding considerations I had not taken into account the correction which HANSEN's value for the obliquity of the ecliptic may need. Nor had I paid heed to the errors in the observed declinations which vary with the declination itself.

<sup>1)</sup> Astron. Nachr. Bd. 144, S. 177.

<sup>2)</sup> I adopt the mean of the results found by FRANZ in two different ways.

The latter would have required a special investigation of those observations, which I did not intend. As to the former point too little certainty seemed to exist. For although the obliquity of the ecliptic adopted finally by NEWCOMB has for the 2<sup>nd</sup> part of the 19<sup>th</sup> century values which are larger by 0".2—0".3 than those from HANSEN, yet the value derived directly by NEWCOMB from the observations of the sun only agrees well with HANSEN for this period.

We have:

	1860	1900
	23°27'	23°27'
HANSEN	26"74	8"03
NEWCOMB	27.00	8.26
NEWCOMB Sun	26.81	7.97

On closer consideration, however, we see that we ought not to use the absolutely most probable value of the obliquity, but that it is best to adopt for each series of observations of the moon the value which is derived from the observations of the sun which have been made at the same time and with the same instrument and have been reduced in the same way. For it may be easily seen that in this way we eliminate for the greater part the errors in the refraction, the flexure of the instrument etc. Some systematic errors, namely those depending on the conditions of the observations which are different for the sun and for the moon will be retained undiminished in the results, yet I hold the course proposed here for the best, unless elaborate researches on the errors of the observations have been made. In this way, at any rate we may get some insight into the influence which the values adopted for the reduction elements of the observations have on the elements derived for the plane of the moon's orbit.

20. For the periods discussed by NEWCOMB and by myself we must therefore find the values of the obliquity of the ecliptic which follow directly from the observations as they are given in the Annals of Greenwich and of Washington.

For Greenwich I could use the resulting values given for each year in the *Greenwich observations* and derive from them the corrections of HANSEN's obliquity. For 1895—1902 these corrections were combined into one mean, but the period 1862—1874 was divided into two parts: 1862—67 and 1868—74, because in the year 1868 STONE's refraction constant had come into use, which is smaller by about 0.5% than that of BESSEL. There are also differences between

the values adopted for the flexure of the instrument in the different years, particularly between those before and after the piercing of the cube in the autumn of 1865, but these differences are neutralized for the greater part by the different values which are adopted for the so-called *R—D* correction, and therefore I thought best not to make more subdivisions. In this way I found :

Greenwich	$\delta \varepsilon$ HANSEN
1862—1867	+ 0".41
1868—1874	— 0 .22
1895—1902	+ 0 .31

For Washington I could only use the values given by NEWCOMB in his *Astronomical Constants* p. 31. I supposed that the values given there for  $\delta' \varepsilon$ , if again I subtracted from them the reduction to the "Pulkowa refraction", would agree with those which follow immediately from the results in the *Washington observations*<sup>1)</sup>. In this way I found :

Washington	$\delta \varepsilon$ HANSEN
1862—1874	— 0".02.

Hence the corrections which must be applied to the obliquity of the ecliptic according to HANSEN become :

1862—1867	$\delta \varepsilon = + 0".20$
1868—1874	— 0 .12
1895—1902	+ 0 .31

The results of FRANZ cannot be corrected in this way. I assumed for them, according to NEWCOMB's final formula  $\delta \varepsilon = + 0".24$ .

We now can determine directly the influence of these corrections on the coefficients of  $\sin u$  and  $\cos u$  derived from the observations.

For we have as a sufficient approximation :

$$\begin{aligned} d \delta &= \cos \varepsilon \sec \delta \sin l d \varepsilon = 0.96 \sin l d \varepsilon \\ &= 0.96 (\cos \theta \sin u + \sin \theta \cos u) d \varepsilon \end{aligned}$$

and the corrections that must be applied to the coefficients *b* and *c* are therefore  $+ 0.96 \cos \theta d \varepsilon$  and  $+ 0.96 \sin \theta d \varepsilon$  respectively.

Hence we find as the corrected values of *b* and *c* :

<sup>1)</sup> I could not make out this with certainty from the succinct discussion in the *Astr. Const.*, and, as it is well-known, a more detailed publication of these important researches was frustrated by circumstances.

	$b$	$c$
1862—64	+0 <sup>u</sup> .54	+0 <sup>u</sup> .44
1865—66	+0.08	+0.51
1867—68	-0.04	+0.25
1869—70	+0.54	+0.52
1871—72	0.15	-0.48
1873—74	-0.72	+0.33
1892	-0.27	+0.90
1895	-0.47	+0.74
1896	+0.08	+0.96
1897	+0.12	+0.87
1898	+0.24	+1.60
1899	+0.78	+0.72
1900	+0.35	+0.61
1901	+0.31	+0.17
1902	+0.52	+0.63

If we examine the values of  $b$ , it appears that the periodic character which before they seemed to reveal, has become much less distinct, while the preceding remarks point to the possibility that also the corrected values of  $b$  and  $c$  may still be affected by sensible systematic errors, for instance by an error of HANSEN's parallax of the moon. For the time being there is therefore no sufficient reason to assume the existence of unknown inequalities in the inclination and the longitude of the node.

The mean results for the two elements then become:

	$\delta i$	$\delta b$	Weight
1868	-0 <sup>u</sup> .08	+ 3 <sup>u</sup> .7	3
1892	+0.28	+10.5	4
1899	-0.25	+ 9.2	3
<b>Mean 1885</b>	<b>-0<sup>u</sup>.10</b>	<b>+7<sup>u</sup>.0</b>	

Hence :

$$\begin{aligned} \text{Correction of the centennial motion of the node} &+ 13'' \\ \delta\theta \text{ 1900} &+ 9''.0 \end{aligned}$$

If for the constant of the moon's parallax we accept, instead of HANSEN'S value, that of NEWCOMB which is larger by  $0''.41$ , the corresponding variation in the  $\Delta\delta$  becomes  $-0''.41 \sin z$  or about:  $-0''.31 + 0''.10 \sin l$ , hence that in the  $b$  and  $c$  respectively:  $+0''.10 \cos \theta$  and  $+0''.10 \sin \theta$ .

We then obtain :

	$\delta i$	$\delta b$	Weight
1868	$-0''.05$	$+ 4''.0$	3
1892	$+0''.21$	$+11.3$	1
1899	$-0''.26$	$+ 8.4$	3
<b>Mean 1885</b>	<b><math>-0''.10</math></b>	<b><math>+ 6.9</math></b>	

Hence :

$$\delta\theta \text{ 1900} \dots \dots + 8''.9.$$

The influence on the final results therefore is immaterial.

**Astronomy.** — "*Contributions to the determination of geographical positions on the West-coast of Africa*". (II). By C. SANDERS. (Communicated by Dr. E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of October 31, 1903).

I. *Determination of the longitude of Chiloango made in the years 1901 and 1902.*

I. In a preceding paper "*Contributions to the determination of geographical positions on the West-coast of Africa*"<sup>1)</sup> I have given some preliminary results obtained for the longitude of Chiloango<sup>2)</sup>. After that time until my temporary return to Europe in the autumn of 1902 I have, as far as possible, continued my observations and extended them to the 2<sup>d</sup> limb of the moon. Lately I have been able to reduce the whole set of observations with all possible accuracy

<sup>1)</sup> Proceedings Acad. Amst. IV, 1901, p. 274.

<sup>2)</sup> Owing to an error in the sign, the results given there for March 3 and May 1 were wrong.

2. *Arrangement of the observations.* On this subject I have said a few words in the paper mentioned. Here I shall consider some points more in detail.

All my observations were made by the method of equal altitudes of the moon and a star. Because of the small latitude of my station ( $\varphi = -5^{\circ}12'$ ) I could make the observations in such positions that the parallel was at small angles with the vertical circle, i. e. that the parallactic angle differed little from  $90^{\circ}$  or  $270^{\circ}$ . Hence the angles of the moon's orbit with the vertical circle were not great either and therefore the accuracy that can be reached by means of observations of the moon was actually attained very nearly, in so far as it depends on the geometrical conditions.

I used my universal instrument described before, and the observations consisted in noting down the moments at which the visible limb of the moon and the comparison star attained the same altitude. The instants of transit over the horizontal threads were determined, first for the one, then for the other object, either combined with readings of the alidade-level. In this way I have obtained 24 observations of the 1<sup>st</sup> limb scattered over 10 nights and 12 observations of the 2<sup>d</sup> limb over 3 nights. I regret that it has not been possible to add to the last number.

The instrument has always been used in the same position, telescope right. In order to prepare myself for the observations I beforehand computed for given moments the azimuth and the zenith-distance of the moon and the star, while the azimuth of the instrument was known by means of the harbour-light<sup>1)</sup>. Each time the level was read just before the transit observations. The reticule has remained in the same position since February 1901<sup>2)</sup>, so that each time the transits could be observed over 7 threads.

The distances between these threads were about  $7^s$ ,  $6^s$ ,  $4^s$ ,  $4^s$ ,  $7^s$ ,  $6^s$  and owing to the rapid succession of the transits and the rather small power of the telescope, I did not succeed in estimating further than the full beats of the chronometer. In future observations it may perhaps be better to sacrifice some transits in order to try to reach a higher degree of accuracy in the others.

Another result of the rapid succession of the separate transits was that I was unable to follow the observed object in azimuth during its transit over the reticule. Hence in some cases it passed in a somewhat oblique direction and while I always took care that the

1) Comp. Contributions to the determination of geographical positions etc. I. p. 3 (276).

2) Ibid. p. 16 (289).

transit over the middle thread should take place very near the middle, the transits over the other threads were observed on either side of it. It may be easily shown, however, that in the present case no appreciable errors can arise from this.

In the first place we shall show that even the errors in the absolute zenith distances generally will be small. By the symmetrical arrangement of the observations, the influence of an inclination of the reticule as a whole will be eliminated from the mean result and the influence of the curvature of the parallel of altitude will always be small for my observations. At a horizontal distance  $c$  from the middle of the field the influence of the curvature of the parallel on the zenith distance is :

$$\Delta z = \frac{1}{2} c^2 \cot g. z \sin 1''$$

Now the proportion of the horizontal to the vertical motion, putting for the parallactic angle  $p$ , is  $\cot g. p$ , and for a transit over a thread at a distance  $f'$  from the middle thread the correction of the zenith distance will be

$$\Delta z = \frac{1}{2} f'^2 \cot g^2 p \cot g z \sin 1''$$

while the extreme threads are at distances of about  $17^s$  or  $250''$  from the middle thread. In one observation, that of 1901 Febr. 25, which owing to the unfavourable relative positions of the moon and the star perhaps had best be excluded, the value of  $\cot g. p$  was 0.68, while for the rest its greatest value amounted to 0.34 and it was generally much smaller. In the most unfavourable case, therefore, we have for the extreme threads  $c = 170''$  and  $\Delta z = 0''.08$ . In all the other observations we have always  $\Delta z < 0''.02$ .

The influence on the difference between the zenith distances of the moon and the star, however, is much smaller still, as the moon and the star always differed little in declination and hence at the moments of the observations were at about the same parallactic angle. The difference between the parallactic angles was, excluding the observation of 1901 Febr. 25, for which  $p - p' = 7^\circ$ , in maximo  $3^\circ$ . So the influence of the curvature of the parallel is almost entirely eliminated in the results of the observations. The same is the case with the influence of the inclination of the individual threads.

That I did not follow the star in azimuth has therefore had no injurious consequences and no corrections are required. On the other hand the consequence may have been that the stability of the instrument during each transit was greater.

After the first object had been observed, the instrument was carefully brought into the azimuth of the second. The difference between the level readings in the two positions was always smaller than 1 division =  $5''.4$  and for 33 of the 36 observations smaller than  $0^d.5$ . The interval between two corresponding transits of the moon and the star was always less than 25 minutes and generally much less.

Finally I remark that, excluding 1901 Febr. 25, the value of the parallactic angle during the observations was always enclosed between  $80^\circ$  and  $110^\circ$  or between  $250^\circ$  and  $280^\circ$ .

3. *Determinations of time. Rates of the chronometer.* Except on 2 nights (1901 Oct. 6 and 13), when I observed transits of stars over the meridian, the corrections of my chronometer to the mean time of Chiloango were always determined by observations of altitude. For this I refer to my previous paper (Contributions I p. (276) 3), where I have also given the corrections of the chronometer and the daily rates for the period 1900 Oct.—1901 July. As, however, I have since been able to correct the observed altitudes for the rather large division errors and the flexure of my instrument (Comp. I. c. p. (285) 12), I once more give in the following table the corrections and the rates for the whole period 1901 Jan.—1902 May. The rates hold for the interval between the date on the line above and that on the same line. In the next column are given the mean temperatures; those for 1902 Jan. 6—Febr. 5 are interpolated values because thermometer readings were wanting. (See table p. 430).

From these data I have derived a formula for the influence of the temperature on the rate. As the differences in temperature are small I could only determine a linear influence. I found:

1901 Jan. 18—Apr. 28	+ 0.91	+ 26°.0
1902 Febr. 5—May 17	+ 1.07	+ 25.8
Mean	+ 0.99	+ 25.9
1901 June 17—Sept. 10	+ 0.19	+ 21.4

hence:

$$\text{Influence of } 1^\circ = + 0.178^1).$$

By means of this temperature coefficient I have reduced all the observed rates to  $+ 24^\circ$  and these reduced rates are given in the

<sup>1)</sup> For this computation too the rate in the interval 1902 April 30—May 12, during which the chronometer was transported to Mayili and back, was used erroneously. If we exclude it, we find for the second summer-rate  $+ 1.05$  at  $26^\circ.0$  and for the temperature coefficient  $+ 0.171$ , which differs little from the value found above.

			M. T.	Chron. Corr.	D. R.	Temp.	D. R. 24°
1901	Jan.	9	6.6	<sup>m</sup> +55 33.65			
	"	18	8.2	39.42	+0.64	24.8	+0.50
	"	25	8.8	45.48	0.82	26.0	0.46
	Febr.	6	8.7	54.98	0.84	25.8	0.49
	"	12	8.4	56 0.76	0.96	26.5	0.51
	"	19	8.2	7 45	0.96	26.0	0.60
	April	17	6.2	57 6.50	0.93	26.0	0.57
	"	19	7.7	2.55	0.83	25.2	0.61
	"	25	9.2	7.73	0.85	26.2	0.45
	"	28	8.0	10.65	0.98	26.1	0.60
	May	9	8.1	19.91	0.84	25.7	0.54
	"	12	8.4	21.38	0.49	25.1	0.29
	"	21	8.2	27.67	0.70	24.7	0.58
	"	22	8.6	28.70	1.03	25.6	0.74
	"	30	8.3	34.74	0.76	24.7	0.64
	June	10	7.6	41.34	0.60	24.1	0.58
	"	17	7.2	45.03	0.53	23.6	0.60
	July	5	7.7	49.90	0.27	21.8	0.66
	"	16	7.8	52.46	0.20	1.0	0.73
	"	25	8.3	54.64	0.28	21.0	0.81
	Aug.	7	8.4	55.54	0.07	21.0	0.60
	"	30	8.0	57.52	0.09	21.2	0.58
	Sept.	10	7.9	58 4.58	0.37	22.4	0.71
	Oct.	6	8.6	9 63	0.31	23.0	0.49
	"	13	8.3	14.38	0.68	23.6	0.75
	"	16	8.1	16.32	0.64	23.3	0.76
	"	17	8.4	17 00	0.68	23.1	0.84
	"	21	8.2	18.87	0.47	23.9	0.49
	Nov.	9	7.9	28.20	0.49	23.7	0.54
	"	16	7.8	33.36	0.74	24.4	0.67
	"	19	7.9	36.32	0.59	25.0	0.81
	"	30	8.0	45.88	0.87	24.8	0.73
	Dec.	5	8.2	48.91	0.61	24.7	0.49
1902	Jan.	6	7.9	59 10.56	0.68	24.6	0.57
	"	25	8.4	22.58	0.63	[24.9]	[0.47]
	Febr.	5	8.0	30.40	0.71	[25.2]	[0.49]
	March	11	8.5	56.74	0.77	25.5	0.50
	"	22	8.5	60 9.58	1.17	26.3	0.76
	"	25	9.7	12 68	1.02	26.5	0.57
	April	10	8.5	32.88	1.26	26.3	0.85
	"	25	8.1	52.51	1.31	26.3	0.90
	"	30	8.3	58.72	1.24	25.7	0.94
	May	12	8.4	61 12.58	1.16	25.2	[0.94]
	"	17	8.8	17.92	1.07	25.6	0.78

last column of the preceding table. There seems to be a slight gradual retardation, but for the rest the reduced rates in the main agree satisfactorily, while some of the most discordant values belong to short intervals. As the lengths of these intervals are very different, it would have little sense to derive a value for the mean discordance.

4. *The reduction of the observations for longitude.* For the reduction of my observations I followed the method given by Prof. Oudemans<sup>1)</sup>.

I also followed his advice not to reduce the transits to the middle thread, but simply to take the mean of the observed times of transit. A slight disadvantage of the course followed by me is that, when either for the moon or for the star the transit over a thread has not been observed, we must also exclude the corresponding transit of the other object. This was only the case with the two observations of 1901 May 21<sup>2)</sup>.

Having found in this way the times of the passage over the mean of the threads we had now first to determine the differences  $\xi$  between the observed differences in zenith distance of the moon and the star as shown by the level-readings and the values computed for them with adopted reduction elements, among which an assumed longitude of the station. Secondly the equations of condition were formed, by means of which the values of  $\xi$  are connected with the variations of the adopted elements. These equations were transformed so as to express  $\Delta L$ , the variation of the adopted longitude, as a function of  $\xi$ , and of the variations of the adopted latitude, of the adopted correction of the chronometer, of the times of transit of the moon and the star, of the adopted right ascension and declination of the two objects and of the adopted values for the parallax and the semidiameter of the moon.

On the one hand this course enabled me to correct the results found provisionally as soon as corrected values of the reduction elements had been derived; on the other hand the equations showed the influence of residual errors in the observed quantities and in the reduction elements.

In the first place I shall consider the values adopted finally for the elements of reduction. I accepted as the latitude of the station  $-5^{\circ} 12' 4''.0$  (Contributions I p. (284) 11). The corrections of the

<sup>1)</sup> Versl. en Med. Kon. Akad. Amsterdam 6, 1857, p. 25—40.

<sup>2)</sup> By using only corresponding transits we also eliminate the influence of the refraction.

chronometer were found by direct interpolation between the observed values as given in the table above. As the temperature varied only slowly I deemed it unnecessary to account especially for its influence. The right ascension and declination of the comparison stars were taken from the ephemerides of the nautical almanac which for these years are based on NEWCOMB'S Fundamental Catalogue and for my purpose could be considered as absolutely correct. This is not the case with the right ascension and declination of the moon, as the errors in the values computed by means of the tables of HANSEN-NEWCOMB may still be quite sensible.

Especially with a view to my observations, E. F. VAN DE SANDE BAKHTYZEN has undertaken an investigation of the errors of those tables<sup>1)</sup> and I could avail myself of his results. For the derivation of the corrections that must be applied to the moon's places I, on his advice, proceeded as follows.

Let us first consider the errors of the longitude. For the constant part of the correction of the mean longitude I adopted  $+ 2''.20$  (BAKH. I p. 376 and 383) and to this I added the corrections for the parallactic inequality etc. computed from the formula of BAKH. I p. 375. The sums of these two corrections were transformed into corrections of the true longitude, and I again added to these the corrections for the inequality in the true longitude which NEWCOMB had been the first to find and which BAKHTYZEN had determined anew from the observations. I used therefor the values of the coefficients  $h$  and  $k$  as given by the formulae in BAKH. II p. 420, but added to either of them the constant correction  $- 0''.30$ , in order better to represent the observations (comp. l.c. p. 416). These corrections should be applied to the orbit longitude, but with sufficient approximation might be considered as corrections of the ecliptic longitude.

As correction of the moon's latitude I adopted (comp. BAKH. II 421),

$$\Delta \beta = - 0''.58 \sin u + 0.086 (\Delta l - 12''.1) \cos u$$

where  $u$  represents the argument of the latitude and  $\Delta l$  the total correction of the longitude, while I assumed for the correction of the longitude of the node for 1902  $+ 12''.1$ .

From the corrections of the longitude and the latitude formed in this way, I derived those of the right ascensions and the declinations by means of the tables in NEWCOMB'S "*Investigation*". Another correction, however, had still to be applied to the right ascensions, the reduction

<sup>1)</sup> E. F. VAN DE SANDE BAKHTYZEN, Investigation of the errors of the tables of the moon of HANSEN-NEWCOMB in the years 1895—1902. I and II. Proc. Acad. Amsterdam Dec. 19th 1903. These two papers I shall quote as BAKH. I and BAKH. II.

from the equinox of the 10 Year Catalogue, for which the errors of the moon had been determined, to that of NEWCOMB'S Fundamental Catalogue from which the positions of the stars were taken. I adopted for this reduction  $+0^s.054$ .

The adopted corrections in  $\lambda$  and  $\beta$  and those in  $\alpha$  and  $\delta$  are given in the following table together with the comparison stars used.

		$\Delta \lambda$	$\Delta \beta$	$\Delta \alpha$	$\Delta \delta$	Star
1901 Jan.	22.2	+1.27	-0.52	+0.446	-0.03	$\epsilon$ Aquarii
	23.3	+1.72	-0.27	.467	+0.42	$\alpha$ Aquarii
"	25.3	+2.80	+0.46	.223	+1.24	$\delta$ Piscium
Febr.	25.3	+4.27	+0.72	.340	+1.56	$\alpha$ Tauri
March	3.3	+4.75	+0.65	.371	-0.90	$\alpha$ Leonis
May	4.2	+3.88	-0.22	.290	-4.69	$\alpha$ Virginis
"	21.3	+4.40	+0.89	.347	+0.53	$\delta$ Geminorum
"	23.3	+4.85	+0.71	.387	-0.56	$\alpha$ Cancri
July	22.3	+4.47	-0.26	.327	-4.94	$\alpha$ Virginis
Nov.	47.3	+2.38	-0.57	.221	+0.42	$\beta$ Capricorni
1902 Jan.	24.4	+3.54	+0.57	.297	-0.42	$\alpha$ Cancri
March	25.3	+3.42	-0.59	.234	-4.73	$\alpha$ Virginis
April	23.3	+2.84	-0.87	.221	-4.70	$\alpha$ Librae

For the moon's parallax I have provisionally adopted HANSEN'S constant, while for the computation of the corrections for parallax BESSEL'S elements of the figure of the earth were used. The correction of HANSEN'S constant is still uncertain and at any rate not large. It will appear moreover that its influence is eliminated to a great extent in the final result because observations have been made as well before as after the meridian passage.

The value for the moon's diameter corresponding to my mode of observation must naturally be derived from my observations themselves by comparing the results for the first and the second limb.

In the following table I shall give a summary of the results obtained. The 2<sup>d</sup> and 3<sup>d</sup> columns contain the values of  $\zeta$  and of  $\Delta L =$  correction of the assumed longitude —  $48^m 32^s.0$  each computed by means of the moon's places of the Nautical Almanac, but, with the values finally adopted for the other reduction elements. The

4<sup>th</sup> and 5<sup>th</sup> columns contain the corrections of  $\angle L$  resulting from the adopted corrections of the right ascension and the declination of the moon, the 6<sup>th</sup> contains the corrected values of  $\angle L$  and the 7<sup>th</sup> the mean results for  $\angle L$  from the observations of each day. The last column shows the derivatives of the longitude relatively to the corrections of the chronometer. The derivatives relatively to the other elements are omitted to save room. I shall only give hereafter their mean values for the observations of each limb. (See table p. 435).

Now the question arises what weights must be assigned to these results and how they will be best combined.

First it must be borne in mind that in 1901 January the transits were observed over 2 threads only and in all the following observations over 7, except in two cases over 6 threads. Therefore we have assigned the weight  $\frac{1}{2}$  to the first mentioned observations. Secondly we must pay attention to special unfavourable circumstances during the observations, and then we find that for that of 1902 Jan. 24 the star was only faintly visible through the hazy atmosphere, and that for the first observation of 1902 March 25 an uncertainty prevails about one of the level-readings. To these observations also the weight  $\frac{1}{2}$  was assigned<sup>1)</sup>.

Finally we had to pay heed to unfavourable geometrical conditions for some observations, which might highly increase the influence of some reduction elements, and also to special cases of uncertainty in one of those elements. I have already mentioned that on 1901 Febr. 25 the observation had been made with very unfavourable relative positions of the moon and the star. The values of the parallactic angle were for the moon and the star  $124^\circ$  and  $117^\circ$  respectively, while in the other cases the most unfavourable value was  $108^\circ$  and the greatest difference between the values for the moon and the star amounted to  $3'$ . We now see that owing to this the derivative relatively to the chronometer-correction is exceptionally large, while also those relatively to the latitude of the station and to the moon's declination have the largest value here.

A special uncertainty on certain days can only be expected in the chronometer-correction. A measure for this uncertainty is given by the interval between the observation of the moon and the nearest time-determination, and it appears that this interval for almost all the observations lies between 0 and 3 days, but for 1901 Febr. 25 amounts to 6 and for 1901 March 3 to 12 days. Another time-determination had still been made on Febr. 28

<sup>1)</sup> This has been taken into account in the derivation of the mean result for March 25 in the table above.

## RESULTS.

Date.	$\zeta$	$\angle L$	Corr for $\zeta$ Moon	Corr. for $\varphi$ Moon	$\Delta L$ corr.	Mean $\Delta L$	$dL$ $d\%$
LIMB I.							
1901							
Jan. 22	-7.18	-13.48	-3.99	0.00	-17.17		-0.74
" "	+3.45	+6.35	-3.99	0.00	+2.36	-7.40	-0.77
" 23	+4.55	+8.53	-4.67	+0.07	+3.93	+3.93	-0.78
" 25	+3.82	+7.59	-6.42	+0.53	+1.70		-1.02
" "	+3.46	+6.85	-6.39	+0.50	+0.96		-1.02
" "	+4.02	+7.91	-6.38	+0.48	+2.01		-1.02
" "	-3.75	-7.35	-6.35	+0.47	-13.23	-2.44	-1.03
Febr. 25	+2.05	+4.60	-8.85	+1.99	-2.26	-2.26	-5.49
March 3	-5.37	+11.94	-12.03	+0.35	+0.26		-0.48
" "	-5.06	+11.44	-12.19	+0.42	-0.33		+0.02
" "	-6.92	+16.01	-12.37	+0.50	+4.14	+1.36	-0.29
May 1	-4.58	+9.86	-9.22	+0.05	+0.69	+0.69	-0.72
" 21	+4.69	+8.20	-8.26	+0.24	+0.08		+0.03
" "	-4.06	-4.86	-8.39	+0.22	-10.03	-4.98	-0.02
" 23	+4.42	+2.65	-10.09	-0.32	-7.76		-0.56
" "	+2.90	+5.42	-10.22	-0.29	-5.09	-6.42	-0.59
July 22	+7.83	+16.99	-0.44	+0.25	+6.80		-0.61
" "	+8.44	+17.56	-10.40	+0.20	+7.36		-0.64
" "	+6.42	+13.14	-10.36	+0.15	+2.93	+5.70	-0.67
Nov. 17	+2.55	+4.94	-6.19	-0.03	-1.28		-0.43
" "	-3.14	-6.09	-6.22	-0.02	-12.33		-0.46
" "	+4.36	+8.48	-6.25	-0.02	+2.21		-0.61
" "	+2.78	+5.82	-6.28	-0.01	-0.47		-0.52
" "	+4.00	+7.84	-6.31	-0.01	+1.52	-2.07	-0.55
LIMB II.							
1902							
Jan. 24	0.00	0.00	-8.43	+0.20	-8.23	-8.23	-0.67
March 25	+0.86	-1.76	-7.10	+0.11	-8.75		-0.78
" "	-8.06	+16.51	-7.08	+0.07	+9.50		-0.76
" "	-3.47	+7.08	-7.06	+0.04	+0.06		-0.72
" "	-2.03	+4.14	-7.03	-0.01	-2.90		-0.72
" "	-4.64	+9.41	-7.01	-0.04	+2.36	+1.03	-0.69
Apr. 23	-5.17	+10.50	-6.49	-0.14	+3.87		-0.73
" "	-1.86	+3.78	-6.47	-0.19	-2.88		-0.72
" "	-6.51	+13.17	-6.45	-0.24	+6.48		-0.70
" "	-3.75	+7.57	-6.43	-0.30	+0.84		-0.69
" "	-4.62	+9.32	-6.40	-0.36	+2.56		-0.68
" "	-4.52	+3.06	-6.38	-0.42	-3.74	+1.19	-0.66

but the resulting chronometer-correction: Febr. 28  $8^h.4 + 56^m 15^s.53$  is somewhat uncertain.

After due consideration of all these circumstances, I have entirely rejected the observation of Febr. 25; to the 3 observations of March 3, however, I have ultimately assigned full weight. For the derivatives relatively to the chronometer-correction for March 3 are very small and their mean value is only  $+ 0.04$ , while on the other hand the chronometer-correction for March 3 changes only  $0^s.26$ , if the time-determination of Febr. 28 is taken into account.

This being established, we had still to find in what way the separate results had to be combined. We had first to investigate whether constant errors had to be feared for the results of the same night. On the one hand I therefore derived mean results for each limb by combining the separate observations with the accepted weights and from the discordances found I computed the mean error of a result with weight 1. On the other hand I determined the mean error free from the influence of the constant error of the night by comparing the separate results with the mean result of the night for those nights in which more than 3 observations had been made.

In this way I found for weight 1, i. e. for the result of one observation without special uncertainty:

Total mean error	Limb I $\pm 5^s.65$
"    "    "	"    II $\pm 4^s.84$
Partial .. ..	. . . . . $\pm 5^s.23$

Although the last value is very uncertain, there seems to be no reason to assume in the results of the final reduction errors that remain constant during the same night. Hence in deducing the final results we need not ask in which night the observations have been made.

In this way we shall now derive for each limb the mean value of  $\angle L$  and also those of the derivatives of the longitude respectively to the other variable quantities. Let us put for the variations of the latitude of the station, of the chronometer-correction, of the chronometer-time of transit of the moon, of its right ascension, of its declination, of its parallax and of its semidiameter:  $\angle q$ ,  $\angle \theta$ ,  $\angle t$ ,  $\angle a$ ,  $\angle d$ ,  $\angle \alpha$  and  $\angle R$  and let  $\angle l'$ ,  $\angle a'$ , and  $\angle d'$  be the corresponding quantities for the star. Then we obtain:

$$\begin{aligned} \text{I } \angle L = & - 18.08 - 0.03 \angle q - 0.48 \angle \theta + 28.05 \angle t \\ & 28.53 \angle l' - 29.05 \angle a + 28.53 \angle a' + 0.02 \angle d \\ & 0.00 \angle d' + 0.86 \angle \alpha + 2.00 \angle R \dots \text{Weight } 19.5 \end{aligned}$$

$$\begin{aligned} \text{II } \angle L = & + 0.70 + 0.01 \angle q - 0.71 \angle \theta + 28.51 \angle t \\ & 29.22 \angle l' - 29.51 \angle a + 29.22 \angle a' + 0.06 \angle d \\ & 0.06 \angle d' - 1.72 \angle \alpha - 2.03 \angle R \dots \text{Weight } 11 \end{aligned}$$

The variations  $\Delta L$ ,  $\Delta \theta$ ,  $\Delta t$ ,  $\Delta t'$ ,  $\Delta a$  and  $\Delta a'$  are expressed in seconds of time, the other ones in seconds of arc, and the derivatives are formed accordingly. Naturally the terms in  $\Delta \theta$ ,  $\Delta t$ ,  $\Delta t'$ ,  $\Delta a$ ,  $\Delta a'$ ,  $\Delta \theta$  and  $\Delta \theta'$  now can only relate to constant errors in these elements. The  $\Delta \pi$  and  $\Delta R$  of the separate equations rigorously express the variations of the parallax values and semidiameters for the actual distances, but might approximately be considered as those of  $\pi_0$  and  $R_0$ , the parallax-constant and the semidiameter, for distance 1<sup>1)</sup>.

We now perceive that the influence of an error in the latitude is very slight and that this is also the case with constant errors in the declination of the moon or the stars. An equinox-error common to the moon and the stars is not entirely eliminated, but its influence is immaterial and my personal error in transit observations, which influences  $\theta$ ,  $t$  and  $t'$ , is eliminated in so far as the error is the same for the moon and the stars. The only terms which we have to consider further are therefore those depending on  $\Delta \pi$  and  $\Delta R$ .

If we accept for the two limbs as mean error for weight I  $\pm 5^s.65$  and  $\pm 4^s.84$  respectively, as it may be that indeed the observations of the second limb are a little more accurate, then we have:

$$\text{I } \Delta L - 0.86 \Delta \pi_0 - 2.00 \Delta R_0 = -1^s.08 \pm 1^s.28$$

$$\text{II } \Delta L + 1.72 \Delta \pi_0 + 2.03 \Delta R_0 = +0^s.70 \pm 1^s.46$$

The mean of the two results without regard to their weights is:

$$\Delta L + 0.43 \Delta \pi_0 + 0.02 \Delta R_0 = -0^s.19 \pm 0^s.97$$

and the resulting longitude found in this way, apart from the fact that it is not wholly free from personal error, is affected only by the uncertainty in the constant of the parallax. If instead of HANSEN'S constant we adopt that of NEWCOMB (*Astronomical Constants* p. 193) which is larger by 0".4, our result becomes:

$$\Delta L = -0^s.36 \pm 0^s.97$$

Hence we see that the influence of the uncertainty in the constant of the parallax is probably not great.

As my final result I accept  $\Delta L = -0^s.3$ , and hence:

LONGITUDE OF THE OBSERVATIONPIER

$$L = -48^m 32^s.3 \pm 1^s.0$$

<sup>1)</sup> If the coefficients of  $\Delta \pi_0$  and  $\Delta R_0$  are determined rigorously we find: for limb I  $+0.83$  and  $+1.93$ , for limb II  $-1.66$  and  $-1.95$ , or practically the same values as formerly (*added 1904 Jun*).

Besides we find by subtracting the two equations:

$$+ 2.58 \Delta \sigma_0 + 4.03 \Delta R_0 = + 1''.78 \pm 1''.94$$

or

$$\Delta R_0 + 0.64 \Delta \sigma_0 = + 0''.44 \pm 0''.48$$

and

$$\text{for } \sigma_0 \text{ HANSEN } \dots \dots \Delta R_0 = - 0''.44$$

$$\dots \text{ NEWCOMB } \dots \dots \dots = + 0''.18$$

or the semidiameter corresponding to my observations does not differ much from that of HANSEN.

As to the accuracy reached in my observations we find as mean error of an observation over 7 threads without special uncertainty, as it is derived from the observations of the two limbs:

$$M. E. = \pm 5^s.39.$$

With this mean error we may compare the one found by Prof. OUDEMANS for the analogous observations made by S. H. and G. H. DE LANGE at Batavia<sup>1)</sup> and that derived by AUWERS from several longitude determinations made by FLEURIJS by means of moon-culminations<sup>2)</sup>

$$\text{DE LANGE 1851—54} \quad M. E. \text{ of 1 obs.} \quad \pm 5^s.25$$

$$\text{FLEURIJS 1867—70} \quad M. E. \text{ of average obs.} \quad \pm 3^s.14$$

The value for FLEURIJS is the mean of the results from the observations at 9 stations. In comparing these results it should be borne in mind that the two instruments and especially that of FLEURIJS were more powerful than mine. On the other hand it was more difficult to derive accurate places of the moon for the years 1851—54.

Finally I shall reduce my result to the harbourlight and to the flagstaff of the residence at Landana. By means of the triangulation mentioned before<sup>3)</sup> I found as differences of longitude:

$$\text{Harbourlight — Observationpier} = + 0^s.22$$

$$\text{Flagstaff — " } = - 1.48.$$

Hence the longitudes from Greenwich become:

$$\text{LONGITUDE HARBOURLIGHT} = 48^m 32^s.1 \pm 1^s.0$$

$$\text{LONGITUDE FLAGSTAFF} = 48^m 33^s.8 \pm 1^s.0$$

The English Admiralty-chart gives for the longitude of the harbourlight  $12^{\circ} 8'$  East =  $48^m 32^s$ .

## II. *Determination of the geographical position of Mayili.*

5. Mayili, a factory of the firm HATTON and COOKSON is situated

<sup>1)</sup> J. A. G. OUDEMANS, Verslag van den geographischen dienst in Nederlandsch-Indië, 1858—1859, Batavia 1860.

<sup>2)</sup> Astron. Nachr. Bd. 108, p. 313.

<sup>3)</sup> Contributions I p. (287) 14.

on the left bank of the Chiloango river a little below the confluence of the Luali and Loango rivers.

In May 1902 I had an opportunity for making here a latitude determination and for determining the difference of longitude with Chiloango.

My instrument was mounted on a heavy wooden tripod, made especially for the purpose, which secured sufficient stability. The observations, however, were very difficult, owing to myriads of insects which made it almost impossible for me to hear the beats of the chronometer.

On May 3 I made the first time-determination, on May 4 I observed the circummeridian altitudes of  $\beta$  Ursae Majoris and  $\lambda$  Centauri for the determination of the latitude and lastly on May 7 I made a second time-determination.

6. *Determination of the latitude.* The two stars used for the determination of the latitude culminated at zenith distances of  $62^{\circ}.0$  North and  $57^{\circ}.4$  South. At each of them 8 pointings have been made, 4 in either position, and so that the last pointing was made in the same position as the first and that they were made on either side of the meridian.

As run-correction for the mean of the two microscopes I applied per  $10' + 2''.0$ . The value of a level-division was put at  $5''.4$  as before and the refraction was computed from BESSEL's tables.

Here follow the results obtained. For each star 4 results have been formed from the 4 pairs of pointings. To the means of those 4 results corrections for division error and flexure have been applied, derived from the formulæ computed before. The circle was at zenith-point  $0^{\circ}$ .

RESULTS FOR THE LATITUDE.

$\beta$ <i>Ursae majoris</i>	- $5^{\circ}4' 39''.46$	
	48.20	
	44.23	
	46.59	
Mean	— $5^{\circ}4' 44''.62$	
Corrected . . . . .		- $5^{\circ} 4' 40''.2$
$\lambda$ <i>Centauri</i>	$5^{\circ}4' 36''.08$	
	35.50	
	33.76	
	36.92	
Mean	— $5^{\circ}4' 35''.57$	
Corrected . . . . .		— $5^{\circ} 4' 40''.3$

The two corrected results agree nearly exactly, while also the mean of the uncorrected results  $-5^{\circ}4'40''.1$  differs only very little from them.

I therefore accept :

$$\text{Latitude of MAYILI} \quad \varphi = -5^{\circ} 4' 40''.$$

7. *Determination of the longitude.* The time-determination of May 3 was made by the observation of Sirius in the West, that of May 7 by the observation of Sirius in the West and of  $\alpha$  Virginis in the East. Unfortunately in the observation of May 3 one of the level readings is uncertain.

The reduction by means of the final value for the latitude, correcting the circle readings for division error and flexure, gave the following corrections of the chronometer *to the mean time of Mayili*:

	Chronom. corr.	D. R.
May 3 8 <sup>h</sup> 4	+ 1 <sup>h</sup> 2 <sup>m</sup> 23 <sup>s</sup> .34	
„ 7 6.5	+ 1 <sup>h</sup> 2 <sup>m</sup> 28 <sup>s</sup> .22	+ 1 <sup>s</sup> .22
	28.00	
Mean	+ 1 2 28.11	

For the correction *to the mean time of Chiloango* I obtained before and after the travel to Mayili:

	Chronom. corr.	D. R.
April 30 8 <sup>h</sup> 3	+ 1 <sup>h</sup> 0 <sup>m</sup> 58 <sup>s</sup> .72	
		+ 1 <sup>s</sup> .16
May 12 8. 4	1 12.58	

If from these results we interpolate the corrections for the instants of the time-determinations at Mayili and compare them with those determined there we find:

<i>Mayili East of Chiloango</i> May 3	1 <sup>m</sup> 21 <sup>s</sup> .13
„ „ „ „ „ 7	21.39.

The time-determination of May 3 is, as said before, somewhat uncertain, yet on the other hand it seems better not to reject it altogether, as owing to the two travels and to the fact that the temperature at Mayili was higher by 1 or 2 degrees than that at Chiloango we may not a priori count on the constancy of the rate between April 30 and May 12.

The two results do not differ much and I adopt:

MAYILI EAST OF CHILOANGO	1 <sup>m</sup> 21 <sup>s</sup> .3
LONGITUDE FROM GREENWICH	— 49 <sup>m</sup> 53 <sup>s</sup> .6.

**Physics.** — “A determination of the electrochemical equivalent of silver.” By G. VAN DIJK and J. KUNST. (Communicated by Prof. H. HAGA.

The principal determinations of the electrochemical equivalent of silver have yielded the following values:<sup>1)</sup>

MASCART	0,011156	1884
F. and W. KOHLRAUSCH	0,011183	1884
LORD RAYLEIGH and MRS. SIDGWICK	0,011179	1884
PELLAT and POTIER	0,011192	1890
KAHLE	0,011183	1898
PATTERSON and GUTHE	0,011192	1898
PELLAT and LEDUC	0,011195	1903

The difference in these numbers is due, partly to the method of the determination of the strength of the current, partly to the way of constructing and using the voltameter.

In most of the investigations the strength of the current was measured by means of an electro-dynamometer in some form or other, either directly or indirectly with the aid of a standard cell (cell of CLARK). F. and W. KOHLRAUSCH used a tangent galvanometer.

For the voltameter the circumstances differed as to the composition and the concentration of the electrolyte, the shape, the dimensions and the composition of the cathode, the way of washing and drying the silver deposit.

The “Bedingungen unter denen bei der Darstellung des AMPÈRE die Abscheidung des Silbers stattzufinden hat” are inserted in the “Reichsgesetzblatt” of May 6, 1901, p. 127<sup>2)</sup> among the regulations of the law concerning the electric units sub § 5*a*.

In connection with the rather considerable difference between the values found for the electrochemical equivalent of silver, a new investigation as to the value of this quantity in which the above mentioned conditions are followed, did not seem to be superfluous to us. The tangent galvanometer has been chosen for the measurement of the strength of the current. Owing to the high degree of accuracy with which the constant of this instrument, and the hori-

<sup>1)</sup> MASCART. Journ. de Phys. (2) 3, p. 283, 1884. F. and W. KOHLRAUSCH. Wied. Ann. 27, p. 1, 1886. LORD RAYLEIGH and MRS. SIDGWICK. Phil. Trans. 2, p. 411, 1884. PELLAT and POTIER. Journ. de Phys. (2) 9, p. 381, 1890. KAHLE. Wied. Ann. 67, p. 1, 1899. PATTERSON and GUTHE. The Phys. Review 7, p. 251, 1898. PELLAT and LEDUC. Compt. Rend. 136, p. 1649, 1903.

<sup>2)</sup> Also Zeitschr. f. Instrumentenk. 6 Heft. 1901, p. 180.

zonal intensity of the terrestrial magnetism and its space- and time-variations may be determined, this method is very well adapted for a laboratory, which has been built without iron and in a place, where no vibrations or stray currents in the earth are to be feared.

*Determination of the horizontal intensity of the terrestrial magnetism : II.*

To this purpose we have followed the bifilarmagnetic method of F. KOHLRAUSCH (Wied. Ann. 17, p. 737, 1882). The absolute bifilar magnetometer was fastened at the top of a high wooden tripod, 90 c.m. to the north and to the south of it the tangent galvanometers were erected on pillars of freestone cemented on the bottom with plaster. The dimensions of the magnetometers of these galvanometers are about the same as those of the "Elfenbeinmagnetometer" of KOHLRAUSCH, but they differ from it in an important detail. The needle with the mirror of the "Elfenbeinmagnetometer" oscillates within a small cylindric space, whose sides are only a few millimeters apart and parallel to the plane of the mirror. In this way the damping has been obtained. The local influence of the instrument is nearly exclusively determined by the magnetic or diamagnetic properties of the material of which the front and back sides consist, which is usually glass. In consequence of the small distance between the needle and the glass walls this influence is variable with their relative position. This renders the magnetometer in this form unsuitable for observations which require a somewhat longer time, as we are not sure of a constant position of the needle. It is therefore that we have modified the instrument in such a way that the distance of the needle from the fixed parts of the apparatus is large enough, the damping being obtained in another manner. The space in which needle and mirror oscillate is a vertical, thinwalled turned cylinder of wood with an internal diameter of 4 c.m. The frontwall has been pierced and round the hole a rim has been cemented in which the glass front fits. A vane of mica is suspended on the cross, which supports the mirror and to which the needle is riveted. This wing can move in a narrow space which is found in the base of the instrument and whose width amounts to a few m.m. In this way a strong air-damping has been obtained.

In order to determine the local influence the magnetometer was turned round the needle, sometimes in positive and sometimes in negative direction; each time over an angle of  $5^\circ$ . Before the mirror a telescope with a scale was placed, and the distance had been

regulated such, that turning an angle of  $5^\circ$  corresponded to 50 cm. of the scale. From different series of observations, in which the variations of the declination were read from another magnetometer, it appeared that turning an angle of  $+5^\circ$  or  $-5^\circ$  from the position of equilibrium caused a deviation of the mirror from  $+0,003$  c.m. to  $-0,002$  c.m. for one of the magnetometers and from  $+0,003$  c.m. to  $-0,007$  c.m. for the other. (The sign  $+$  indicates that the turning of the mirror and of the magnetometer are in the same direction.) These numbers are the mean values of a series of usually 10 observations. The needle had a different position in different observations, either more forward or more backward; no fixed relation between the deviation and the place of the needle could be observed. We have equated the local influence to zero; the error ensuing from this will not amount to more than to some hundredthousandths.

A rectangular turned copper ring 8,4 m.m. large and 3,6 m.m. thick, supported by a wooden frame formed the circuit of the tangent galvanometer, which was placed south of the bifilar magnetometer. It resembles the apparatus described by KOHLRAUSCH *Wied. Ann.* 15, p. 552, 1882.

The circuit of the tangent galvanometer placed to the north was formed by a copper wire of 0,059 cm. diameter, tightly strained round a marble disc; the magnetometer can be placed in a triangular opening, which is cut out of the disc.

In order to determine the local influence, the magnetometer was supported free from the other part of the tangent galvanometer and this was turned over an angle of  $30^\circ$  round it to either side. We found that turning the marble galvanometer from  $+30^\circ$  to  $-30^\circ$  caused a deviation of the mirror in one series of  $-0,002$  cm., another time of 0,000 cm. For the other galvanometer this deviation amounted to  $+0,004$  cm. This difference may be ascribed to experimental errors, and therefore no influence of the instrument exists here either.

The ratio of the values of  $H$  at the place where the bifilar magnet, and at those where the needles of the magnetometers were suspended, was determined with the local-variometer of KOHLRAUSCH; a bifilar variometer indicated the time-variations of  $H$ .

From the observations with the local-variometer — the corrections for the time-variations being applied — the ratio of the values of the intensity of the magnetic field was derived as the average value of a series of numbers, whose extreme values differed less than  $\frac{1}{10000}$ .

The ratio of  $H$  at the places of the bifilar magnet and of the

needles inside the magnetometers may be deduced from these data.

The distance between the suspension-wires above and below, the length of the wires and the weight which they support, are of primary importance for an accurate determination of the value of  $H \times M$  for the bifilar magnetometer ( $M =$  magnetic moment of the magnet). The wires run above and below closely along two small scales divided in  $\frac{1}{2}$  m.m. The distance between the wire and the two adjacent divisions of the scale is determined by a microscope with ocular scale. (1 m.m. corresponds to about 23 divisions of the ocular scale) and the distance between the divisions of the two scales is determined with a comparator. The distance is about 12.4 cm. These measurements have been performed before and after the observations (August 1903); the difference of the distance of the wires found in the two determinations amounted to:

above 0.004 m.m.      below 0.002 m.m.

The mean value of the two determinations has been taken as the distance during the observations. It does not differ more from those values than  $\frac{1}{60000}$ .

The length of the wires has been determined before, after, and a few times between the observations with the aid of a glass scale. The extreme values of the lengths reduced to the same temperature differed 0.13 m.m.; the length of the wires being about 232 cm.

An error of 0.1 m.m. causes an error in the result of  $\frac{1}{46000}$ .

The pieces, suspended on the wires are: the horizontal cross-bar with its vertical rod and the bearer of the magnet which are made of aluminium, the magnet, and a vane of mica in diluted glycerin for the damping. These different pieces (with the exception of the mica-vane) have been weighed separately and together; the difference was 1 mgr., the total weight about 160 gr. The weight of the mica-vane with its suspension-wire, immersed in the liquid so far as during the observations, was determined at: before the observations, 1.444 gr., afterwards 1.457 gr., average value 1.450 gr. The error which may ensue from this difference is not great: a difference of 7 mgr. gives an error of  $\frac{1}{46000}$  in the result.

In order to determine the value of  $\frac{M}{H}$ , we must measure the polar distance of the magnet and the distance of the centers of the needles.

The polar distance of the magnet, 16.06 cm. long, was derived

from the deviations of the magnetometer-needles caused by the magnet when placed normal to the magnetic meridian in two different positions symmetrical with respect to these needles. Two determinations in which the distances were chosen: 80 and 100 cm., and 75 and 105 cm. yielded the values 13,40 and 13,23 cm. The difference may be due to experimental errors. A variation of  $\frac{1}{40}$  m.m.

of one of the distances, causes — *ceteris paribus* — a variation in the value of the polar distance larger than the difference between the two values found. We have taken for the polar distance the mean value 13,31 cm. This agrees fairly well with  $\frac{5}{6}$  of the length. ( $\frac{5}{6} \times \text{length} = 13,38$ ).

In order to ascertain the distance between the centers of the needles, we first determined the difference of their distance from the cocoon silk suspension-fibres. This difference was derived from the deviations of the needles caused by the magnet, as well in one of the positions of the magnetometers as when they had changed place, care being taken that the silk fibres had the same positions both times. In two observations this difference amounted to 0,007 c.m. and 0,009 c.m.: average value 0,008 cm. A difference of distance of 0,001 cm. has an influence on the result of  $\frac{1}{120000}$ .

The distance of the silk fibres was measured by projecting the fibres from two telescopes, 180 cm. apart and at a distance of about 5 m. from the magnetometers, on a horizontal scale placed behind them.

It appeared that the walls of the tube of the magnetometer had no influence on the course of the rays.

We determined the value of  $H$  before and after the time of the passage of the current, in order to arrive at the mean value of  $H$  during that time. During all this time the indications of the local-variometer of KOHLRAUSCH, erected in a room with nearly constant temperature, were read, during the determinations of  $H$  every 2 minutes, in the time between those determinations every 5 minutes.

The value of  $H$  during the passage of the current was derived from the constants of the variometer, the mean reading during the first determination of  $H$  and during the passing of the current and the value of  $H$  found in the first determination of  $H$ . The same calculation was performed with the second determination of  $H$ . The two values found in this way for  $H$  during the passage of the current differed in most cases only  $\frac{1}{9000}$  or not even so much. Only

a few times the difference amounted to  $\frac{1}{6000}$  or  $\frac{1}{4500}$ . The mean of the two values of  $H$  found in this way, was taken as value of  $H$ .

*The tangent galvanometers.*

Five diameters of the tangent galvanometer "north" were measured by comparing them with a standard meter by means of a kathetometer; they differed less than 0,1 m.m. Before the observations we found for the mean value of the external diameter: 41.3833 c.m.  $t = 14^{\circ} 5$ , after the observations we found 41.3842 c.m.,  $t = 17^{\circ} 5$ . Reduction of the former value to the temperature  $t = 17^{\circ} 5$  yields 41.3843 c.m. So the agreement is perfect.

The ring of the tangent galvanometer "south" was not so perfectly circular; moreover its shape was not quite constant. Yet the different determinations yielded mean values for the diameter which agreed very well. Ten diameters have been measured, five on each side, the distances of which were as nearly equal as could be obtained. The values found are:

after the observations	$2 R = 40,445$ cm.	$t = 17^{\circ} 3$
before the observations	40,443 cm.	$t = 14^{\circ} 5$

a still earlier determination yielded 40,446 c.m. at  $t = 19^{\circ} 8$ . When reduced to equal temperature these values differ much less than

$$\frac{1}{40,000}.$$

For the *determination of the intensity of the current* sometimes one, sometimes the other tangent galvanometer was used. The current was supplied by a battery of 3 or 5 accumulators; resistances of about 20 ohms, two voltmeters, a commutator and one of the galvanometers were inserted in the circuit. The intensity of the current varied between 0.30 and 0.45 ampères, the quantity of silver deposited was about 1 gram; the current passed therefore during 48 or 32 minutes. Half a minute after the current was closed the deflection of the tangent galvanometer was observed for the first time, and further every minute. While the current passed through one of the galvanometers, the variations of the declination were observed on the other. At  $\frac{1}{4}$  and at  $\frac{3}{4}$  of the interval during the passage of the current, the current was reversed; during the short time required for the reversal, a short circuit was formed, so that the current did not pass through the galvanometer; the error arising from this circumstance is however so small, that it cannot have any influence on the result. The influence of the reversal of the current in one

of the galvanometers on the reading on the other may be calculated with a sufficient degree of accuracy from the dimensions of the galvanometer, their mutual distance, and the approximated knowledge of the intensity of the current. Before, after and between the different determinations the two galvanometers were read at the same time in order to ascertain their course. The time was determined with a chronometer, which ticked 120 times a minute, every day it was compared with an astronomical clock of great accuracy.

*The voltameters.*

The cathodes consisted of platinum, two of them were cup-shaped, the third was a cylinder ending in a hemisphere: a silver rod served as anode. In order to intercept particles, which might fall from the anode a SOXILET filtering-paper finger was placed round it, manufactured by SCHLEICHER and SCHÜLL. A 20% neutral solution of  $\text{Ag NO}_3$  formed the electrolyte. This was partly obtained from E. MERCK, Darmstadt, partly from the firm J. W. GILTAY, formerly P. J. KIPP and SOXS, at Delft.

Two voltameters were placed in the circuit in order to ascertain that no irregularities occurred in the deposition of the silver. In most cases the weight of the deposit at the cathode agreed to within 0,1 m.gr., once it amounted to more than 0,2 m.gr. The mean value of the two weights was assumed for the weight of the deposited silver.

The weights used for the weighing had been corrected by testing them to a standard kilogram.

In the same way all scales used for the measurements have been compared with a standard meter, whose divisions are again compared with a standard length of 2 d.m. whose corrections were accurately known.

The distance from the scales to the bifilar magnetometer and the galvanometers was measured with a wooden scale of 3 meters. Marks were made at distances of 1 meter and brass scales divided into m.m. could slide along the ends; these scales ended in points of ivory. For the galvanometers the distance from the scale to the glass front was measured, for the bifilar magnetometer the distance to the mirror. For each observation these distances were measured and also the distance of the silk fibres of the magnetometers. The different corrections for the inclination of the mirror, the thickness of the glass front, the distance from the front to the mirror, etc. were applied to the distance.

The length of the scale of 3 meters proved not to be perfectly

Numero	$H$	$i$	$t$	$p$	$\alpha$ North galvano- meter	$\alpha$ South galvano- meter
1	0.18186	0.039083	2160.05	0.94417	0.011184	
2	0.18187	0.043462	2160.05	1.05014		0.011186
3	0.18156	0.041659	2160.95	1.00647	0.011185	
4	0.18150	0.041711	2160.05	1.00759		0.011183
5	0.18157	0.045681	1920.05	0.96799		0.011184
6	0.18160	0.045481	1920.05	0.97657	0.011183	
7	0.18159	0.039307	2400.06	1.05477		0.011181
8	0.18202	0.038134	2400.06	1.02354		0.011184
9	0.18191	0.038588	2400.06	1.03565	0.011183	
10	0.18160	0.038770	2400.06	1.04007	0.011178	
11	0.18161	0.031629	2880.07	1.01895		0.011183
12	0.18157	0.036271	2640.06	1.07048	0.011179	
13	0.18162	0.036644	2400.06	0.98335		0.011181
14	0.18189	0.030924	2880.07	0.99571	0.011182	
15	0.18170	0.030813	2880.07	0.99248	0.011184	
16	0.18198	0.030284	2880.07	0.97501		0.011179
17	0.18164	0.040637	2160.05	0.98136	0.011180	
18	0.18123	0.043140	2160.05	1.04181		0.011180
19	0.18155	0.033782	2640.06	0.98849		0.011183
20	0.18192	0.037478	2400.06	1.00565		0.011180
21	0.18163	0.039023	2400.06	1.04695	0.011179	
22	0.18140	0.035231	2640.06	1.03997	0.011181	
23	0.18163	0.037327	2400.06	1.00162	0.011181	
24	0.18191	0.037678	2400.06	1.01106		0.011181
Mean value					0.0111816	0.0111821
					$\pm 0.00000066$	$\pm 0.00000060$
					(mean error).	

$H$  denotes the horizontal intensity,  $i$  the intensity of the current,  $t$  the time,  $p$  the weight of the silver-deposit,  $\alpha$  the electrochemical equivalent. All these quantities are measured in c. g. c. units.

constant; it had increased about 0,2 m.m. during the time from before till after the observations. A determination of a part of the length, which was performed between the observations, convinced us that the change had taken place gradually. The mean value of the length before and after the observations is used as the length of the scale for all observations.

This will have but a very small influence on the result; it will cause the first of the values found for the equivalent to be somewhat too large, the last to be somewhat too small. The difference however does not amount to more than  $\frac{1}{16000}$ . The distance from the scales to the galvanometers was about 314,2 cm., that to the bifilar magnetometer about 317,5 cm.

We have made 24 determinations of the electrochemical equivalent of silver. The annexed table (p. 448) shows the results.

The values for the electrochemical equivalent  $a$  deduced from the observations with the different galvanometers differ less than  $\frac{1}{20000}$ . As the mean value of all determinations we find:

$$a = \underline{\underline{0.0111818}} \pm 0.0000004. \text{ (mean error).}$$

In connection with the agreement between the different observations, we are of opinion that this number is accurate to  $\frac{1}{10000}$ .

The observations will be published later in extenso.

*Physical Laboratory, University Groningen.*



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday January 30, 1904.

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CONTENTS.

- W. ALBERDA VAN EKENSTEIN: "Dibenzal- and benzalmethylglucosides." (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 452.
- C. H. SLUJTER: "The transformation of isonitrosoacetophenonsodium into sodium benzoate and hydrogen cyanide." (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 453.
- H. W. BAKHUIS ROOZEBOOM and A. H. W. ATEN: "Abnormal solubility lines in binary mixtures owing to the existence of compounds in the solution", p. 456.
- M. W. BEIJERINCK and A. VAN DELDEN: "On the bacteria which are active in flax-rotting", p. 462. (With one plate).
- J. K. A. WERTHEIM SALOMONSON: "On tactual after-images." (Communicated by Prof. C. WINKLER), p. 481.
- A. SMITS: "The course of the solubility curve in the region of critical temperatures of binary mixtures." (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 484.
- C. A. J. A. OUDEMANS: "Exosporina Laricis OUD. — A new microscopic fungus occurring on the Larch and very injurious to this tree", p. 498. (With one plate).
- P. H. SCHOUTE: "PLÜCKER's numbers of a curve in  $S_n$ ", p. 501.
- JAN DE VRIES: "On systems of conics belonging to involutions on rational curves", p. 505.
- JAN DE VRIES: "Fundamental involutions on rational curves of order five", p. 508.
- C. H. BRINKMAN: "The determination of the pressure with a closed air-manometer." (Communicated by Prof. J. D. VAN DER WAALS), p. 510.
- J. J. VAN LAAR: "On the shape of melting-point-curves for binary mixtures, when the latent heat required for the mixing is very small or = 0 in the two phases", (3rd communication). (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 518 (With one plate).
- W. H. KEESOM: "Isothermals of mixtures of oxygen and carbon dioxide. I. The calibration of manometer and piezometer tubes", p. 532. II. "The preparation of the mixtures and the compressibility at small densities", p. 541. III. "The determination of isothermals between 60 and 140 atmospheres, and between  $-15^{\circ}$  C. and  $\pm 60^{\circ}$  C.", p. 554. IV. "Isothermals of pure carbon dioxide between  $25^{\circ}$  C and  $60^{\circ}$  C. and between 60 and 140 atmospheres", p. 565. V. "Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide", p. 577 and 588. (With 2 plates). VI. "Influence of gravitation on the phenomena in the neighbourhood of the plait-point with binary mixtures", p. 593. (Communicated by Prof. H. KAMERLINGH ONNES).
- H. E. J. G. DE BOIS: "Hysteretic orientatic-phenomena." (Communicated by Prof. J. D. VAN DER WAALS), p. 597.

The following papers were read:

**Chemistry.** — Professor LOBRY DE BRUYN presents a communication from Mr. W. ALBERDA VAN EKENSTEIN on: "*Dibenzal- and benzal-methylglucosides.*"

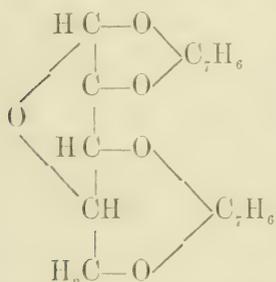
(Communicated in the meeting of December 19, 1903).

While derivatives of formaldehyde may be obtained from sugars by using sulphuric or phosphoric acid as condensing agent<sup>1)</sup> it is also possible to effect the condensation of aromatic aldehydes and ketones with these substances by using phosphoruspentoxide.

In the case of benzaldehyde the desired substances are obtained by mixing two parts of the sugar in a mortar with three parts of the freshly distilled aldehyde and then adding with continuous stirring three parts of  $P_2O_5$ . The clear mass is left for half an hour, then diluted with iced-water and the precipitate is dissolved in methylalcohol.

From this solution the pentosederivatives are obtained as well-crystallised products while the aldohexoses (also fructose and sorbose) yield thick syrups which as yet have not been made to crystallise.

The pentosederivatives contain two benzal-groups and no hydroxyl-group. For this reason their constitution is probably analogous to that of the formal derivatives, for instance.



The hexosederivatives are also formed from two mol. of benzaldehyde; judging from their behaviour towards aceticanhydride they still contain a hydroxylgroup.

It is not improbable that the substances obtained from the hexoses are mixtures of isomers.

When these aldehydederivatives are formed, the carbonylgroups have disappeared as in the case of the compounds derived from formaldehyde; consequently they do not reduce Fehling's solution. The number of benzalgroups may be readily determined by boiling with phenylhydrazine dissolved in dilute acid and weighing the benzalphenylhydrazone which has been formed.

*Dibenzalarabinose*, melting point  $154^\circ$ ,  $[\alpha]_D = +27^\circ$  (in methylalcohol). Found C 69.8, H 5.6. Calculated from  $C_{15}H_{18}O_5$ : C 69.9, H 5.5. Completely hydrolysed by boiling with dilute sulphuric acid; emulsin has no action.

<sup>1)</sup> LOBRY DE BRUYN and ALBERDA VAN EKENSTEIN, Proc. June 28, 1902.

*Dibenzalerylose*, m.p. 130°,  $[\alpha]_D = + 37^{\circ}.5$  (in M. alc.).  
*Dibenzalrhannose*, m.p. 128°,  $[\alpha]_D = + 56^{\circ}$  „ „ „

Of the oily dibenzalhexoses, those derived from mannose, glucose and galactose show a faint right-handed polarisation, but the products obtained from fructose and sorbose are somewhat laevo-rotatory. It has already been noticed that they still retain a hydroxylgroup; these acetylderivatives also have not as yet been obtained in a crystalline state.

The *glucosides* react much more readily with benzaldehyde than the sugars. On dissolving the substances in benzaldehyde and boiling for some hours with addition of a little anhydrous sodiumsulphate, benzalderivatives are formed which are all readily crystallisable substances.

*Monobenzal  $\alpha$ -methylglucoside*, m.p. 158°,  $[\alpha]_D = + 85^{\circ}$ .  
 „ „  $\beta$ . „ „ „ 194°,  $[\alpha]_D = - 75^{\circ}$ .  
 „ „ *methylmannoside*, „ 110°, faint laevo-rotatory  
 Di „ „ „ „ 178°,  $[\alpha]_D = - 5^{\circ}$ .

The last two are formed simultaneously and may be separated by means of hot water.

It must also be observed that other aromatic aldehydes, such as p-totnylaldehyde and cuminol, also enter into combination with sugars; salicylaldehyde cannot react with sugars because it is two readily converted by  $P_2O_5$  into disalicylaldehyde, but its derivatives with glucosides have however already been obtained.

Further particulars of this research will be published more fully later on in the *Recueil*.

*Lab. of the Fin. Dep.* Nov. 1903.

**Chemistry.** — PROFESSOR LOBRY DE BRUYN presents a communication from MR. C. H. SLUITER on: “*The transformation of isonitrosoacetophenonsodium into sodium benzoate and hydrogen cyanide*”.

(Communicated in the meeting of Dec. 19, 1903).

When CLAISEN had discovered his well-known condensation process and had demonstrated for ketones that the hydrogen of the methyl group adjacent to the carbonyl group is readily replaceable, he also found that the isonitrosoketones could be obtained with the aid of amylnitrite and sodium alcoholate <sup>1)</sup>. With MANASSE <sup>2)</sup> he investigated

<sup>1)</sup> Ber. 20. 656.

<sup>2)</sup> Ber. 20. 2194.

the properties of isonitrosoacetophenon:  $C_6H_5COCH:NOH$ . This substance appeared to be a fairly strong acid. The sodium salt suffers a remarkable decomposition into sodium benzoate and hydrogen cyanide when touched with a hot substance, when moistened with a drop of strong acid or when warmed with excess of aqueous soda.



The HCN-molecule is therefore, so to speak removed from the molecule of the sodium salt whilst ONa migrates to the carbonylgroup. CLAISEN further states that after being heated for two days with two mols. of *n*-soda, the sodium salt had been completely converted into sodium cyanide and benzoate.

It was of importance to subject this reaction to a further dynamical research to determine its order and to investigate the influence of the addition of alkali and of a salt and also that of the solvent.

The sodium salt was made according to CLAISEN'S directions. As a perfectly pure salt was required, it was prepared by recrystallising the free isonitrosoderivative from chloroform and neutralising this with the equivalent quantity of sodium alcoholate.

If the salt is dissolved in 70% alcohol, it may be precipitated by addition of ether as a yellowish coloured hydrate containing four mols. of water of crystallisation.

Found: 29.5%  $H_2O$ , calcul.: 29.6%. The salt obtained on drying contained 13.5% of sodium, theory 13.45%. When gently heated the yellow salt loses water and turns orange-red, which is the colour of the anhydrous salt.

After some fruitless efforts to trace the progress of the transformation by titration it was found that this may be accurately done by the aid of the colorimeter, for the aqueous solution of the sodium salt is yellow whilst the decomposition products are colourless.

In the preliminary experiments required for ascertaining the properties of the colorimetric standard liquid, it was found that the colour of the dissolved salt is modified by dilution. The concentrated solutions of the sodium salt have an orange tinge, which turns yellow on dilution; the experiment further showed that, if we work with solutions not exceeding 1%, the diminution in colour may be taken as proportionate to the dilution. This does not hold good for more concentrated solutions; 100 c.c. of a 1% solution is colorimetrically equal to 47 c.c. of a 2% solution and not to 50 c.c.

These phenomena are probably connected with the increasing electrolytic dissociation of the salt on dilution. As the aqueous solution has an alkaline reaction, a perceptible hydrolytic decompo-

sition takes place, the extent of which I will try to determine.

Some preliminary experiments had also shown that temperatures from 50° to 70° lend themselves very well to the determination of the reaction velocity. In carrying out the experiments, a weighed quantity of the salt was dissolved in previously heated water, so that on introducing the solution into the thermostat, the temperature equilibrium was soon reached. At definite times an aliquot part of the liquid was taken from the bottle by means of a pipette, at once strongly cooled and after diluting if necessary to about 1%, it was compared colorimetrically with the standard liquid. As such the liquid which was taken from the bottle the first time, namely on commencing the measurement, was used. Special experiments had shown that at the ordinary temperature the transformation proceeds so slowly that it is not measurable within 24 hours.

The experiment was generally continued until 30 to 40 % of the salt had been converted; at 60° this was the case after 1½ to 2 hours.

It has now appeared that the velocity of decomposition of isonitrosoacetophenonsodium is represented by the equation of the first order; it is unimolecular, since the reaction constant is independent of the concentration. In the case of a 1% solution at 53.6°  $k$  was found to be 0.00062, for a 5% solution  $k = 0.00059$  (time in minutes).<sup>1)</sup> The increase of the reaction velocity with the temperature was shown by the following figures: 1% solution at 60°  $k = 0.0023$ ; at 70°  $k = 0.0048$ <sup>2)</sup>

The influence of a salt with a common ion and that of free alkali is peculiar. That addition of NaCl diminishes the electrolytic dissociation of the sodium salt, was to be expected and may be readily proved colorimetrically, the addition of 1 mol. of NaCl and 1 mol. of NaOH (or 1 mol. KCN) increases the colour of a 1% solution in the proportion of 93 to 100, that of 10 mols. of NaOH in the proportion of 81 to 100.

NaCl and NaOH exert, however, also a retarding influence on the reaction velocity. For a 1% solution and 1 mol. of NaCl  $k = 0.0015$ ; 1/10 mol. NaOH,  $k = 0.0014$ ; 1 mol. NaOH  $k = 0.0015$  whilst for pure water  $k = 0.0023$ . In another experiment, when the transformation had to some extent taken place in pure water, 1/10 mol. of NaOH was added to the liquid and  $k$  then fell from 0.0022 to

<sup>1)</sup> With solutions of a greater concentration the colour after some time gets more pronounced evidently by polymerisation of the HCN formed.

<sup>2)</sup> 0.8% sol. at 69°,  $k = 0.0045$ . The temperature coeff. seems to decrease with increasing temp.; this requires further investigation.

0.0013 (temp. 60.1). If a large excess of NaOH is added from the commencement, the transformation velocity again reaches the same figure as for pure water; for 10 mols. of NaOH,  $k = 0.0022$ .

We are dealing here with a special unknown influence of the added substances; these certainly will modify the concentration of the molecules undergoing change, [either the salt mol. or the acid ion] by the diminution of the electrolytic dissociation, but as the reaction constant is independent of the concentration, this cannot explain the fall of that constant.

In the dry state the salt is more permanent than in solution, for after heating for about  $2\frac{1}{2}$  hours at  $60^\circ$  it was not perceptibly decomposed and gave no odour of HCN. At  $70^\circ$  it turns darker after some time and evolves HCN; the decomposition is then evidently more complicated.

Finally, the decomposition velocity was also determined in methyl- and ethylalcohol; that in ethylalcohol is the smallest whilst methylalcohol stands between water and ethylalcohol. I found at  $60^\circ$  for 1% solution in water 0.0023, in absolute methylalcohol 0.0017, in 97% methylalcohol 0.0018, for a  $\frac{1}{2}\%$  solution in 97% ethylalcohol 0.001, for 50% ethylalcohol 0.0013. Addition of water consequently accelerates the transformation.

The intensity of the colour of a solution containing the same amount of sodium salt is largest for ethylalcohol, smaller for methylalcohol and smallest for water<sup>1)</sup>; this phenomenon is undoubtedly connected with the fact that the electrolytic dissociation of salts in the said solvents increases in the order indicated.

Amsterdam, Dec. 1903.

Org. Chem. Lab. Univ.

**Chemistry.** — Prof. H. W. BAKHUIS ROOZEBOOM presents a communication from himself and Mr. A. H. W. ATEN on: "*Abnormal solubility lines in binary mixtures owing to the existence of compounds in the solution.*"

(Communicated in the meeting of December 19, 1903).

Last year<sup>2)</sup> when engaged in a research on acetaldehyde and its polymer paraldehyde, I investigated the connection between the equilibria of phases of substances which in the liquid and gaseous condition consist of mixtures of two kinds of molecules in equilibrium, and the equilibria of phases in binary mixtures.

<sup>1)</sup> The solubility of the salt in ethylalcohol is also the smallest.

<sup>2)</sup> Proc. Oct. 1903, p. 283.

This investigation is capable of further extension and so we can examine the equilibria of phases in binary mixtures in which the two components form one or more compounds.

Let us limit ourselves to the first case. If an equilibrium exists the quantity of the compound in the liquid or vapour will be dependent on the proportion of the two mixed components and on the temperature and pressure.

We now consider only the equilibria between liquid and solid and this at constant pressure. If the compound is wholly undissociated, the phenomena of melting and solidifying may be represented in space by means of an equilateral triangular prism in which the height represents the temperature and points in the equilateral triangle represent the relative proportions of the components  $a_2$  and  $b_2$  and of the compound.

For convenience we suppose the latter to be  $ab$ . It now behaves as an independent component, as it is supposed that there is no equilibrium between  $ab$ ,  $a_2$  and  $b_2$ . We then obtain, in space, for each of the three solid substances a melting-surface which takes a downward course from the melting point.

Should, however, the compound be in equilibrium with its components, it ceases to be an independent component and at each temperature only those relative proportions can exist in a liquid condition, which are in internal equilibrium.

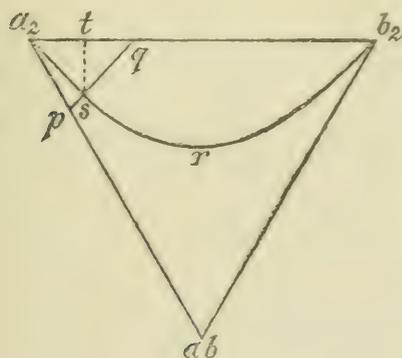


fig. 1.

The curved line  $a_2 r b_2$  in the adjoining figure represents such an equilibrium line, which therefore indicates the only proportions capable of existing at a given temperature. We call this line the dissociation-isotherm.

If the compound did *not* form an equilibrium with its components and if the chosen temperature was situated below the melting point of  $a_2$  a line  $p q$  would then

be the solubility-isotherm for the solid substance  $a_2$  and in the case of an ideal course of the melting-surface of this component  $a_2 p$  would be equal to  $a_2 q$  and the line  $p q$  would be straight. The points of the line  $p q$  then indicate the solutions which can be in equilibrium with solid  $a_2$  at the temperature in question.

If, however,  $a_2 r b_2$  is the equilibrium line of the liquid phase, the point  $s$  will be the only point of the line  $p q$  which can exist

simultaneously with solid  $a_2$  and be also in internal equilibrium.

But if that internal condition of equilibrium is not known we can only determine the gross composition of the liquid as a mixture of  $a_2$  and  $b_2$  and in this way we find the point  $t$  which is the projection of  $s$ .

Acting in the same manner we should obtain for all temperatures the actual composition of the solutions which at various temperatures are in equilibrium with solid  $a_2$  and also their gross composition if we look upon them as binary mixtures built up from  $a_2$  and  $b_2$ .

The same might be determined in regard to the liquids in equilibrium with solid  $b_2$  or solid  $ab$ . This shows that the equilibria of binary mixtures in which a dissociating compound may be formed from the components, must really be looked upon as ternary mixtures with a limiting clause, implied in the dissociation equilibrium in the liquid.

For this reason the form of the solubility-lines which we obtain in the system, considered as a binary mixture, is totally dependent on the manner in which the dissociation in the liquid phase and the melting-surfaces of the components change with a change of temperature.

Guided by these ideas, Mr. ATEN has worked out different theoretically-possible cases which can partly explain abnormal solubility-lines and which point, in addition, to phenomena as yet undiscovered.

Let us first suppose that the compound  $ab$  in the liquid condition is exothermic.

In such a case the dissociation of the compound at first increases but little as the temperature rises, then very much and afterwards again but little. If we draw, in the triangle, a series of dissociation isotherms for equal temperature intervals, these will at elevated temperatures lie close to the side  $a_2b_2$  and will differ but little. Afterwards they will diverge greatly and finally come close together and approach the sides  $a_2ab$  and  $b_2ab$ . In Fig 2, nine such isotherms are shown.

Let us now draw for the same series of temperature the solubility-isotherms of  $a_2$  and assume as the most normal case that they come closer together as the temperature falls (from 9 to 1).

The locus of the intersections of the dissociation- and solubility-isotherms is the projection of the spacial melting-point-curve for  $a_2$ .

By projection on the side  $a_2b_2$  we get the gross composition expressed in  $a_2$  and  $b_2$  and by now plotting temperatures as ordinates we obtain the solubility line  $ABCDEF$  commencing at the melting point  $A$ . The line thus drawn exhibits three portions  $EF$ ,  $FC$  and  $CBA$  which, particularly in the case of many salts, have been

repeatedly met with in different combinations and of which the middle part is particularly interesting because here the solubility of the component  $a_2$  decreases with an increase of temperature.

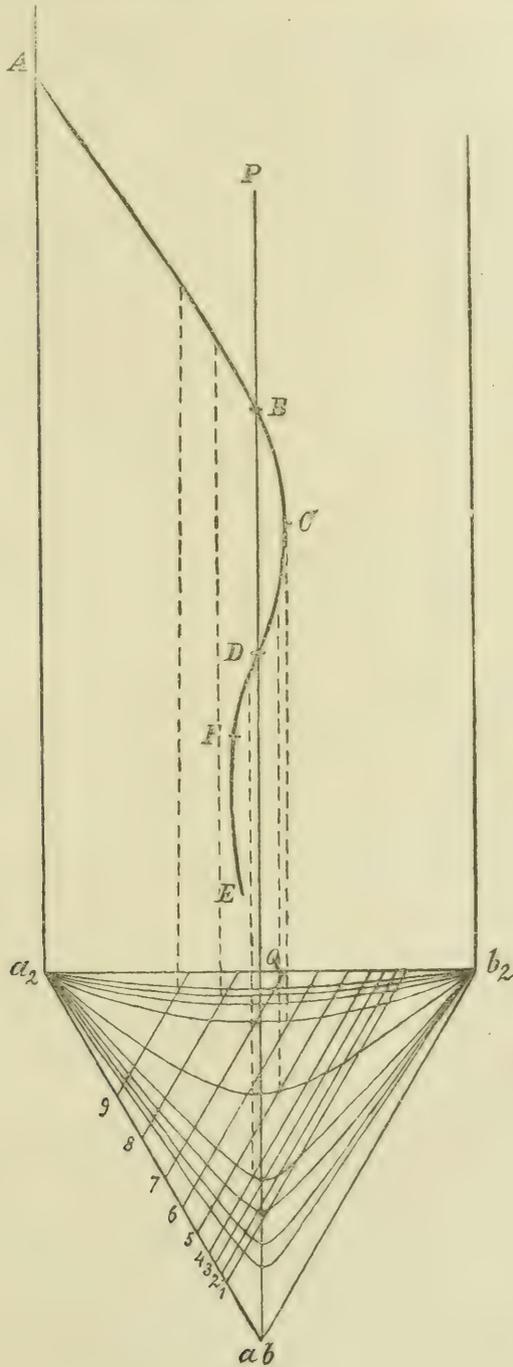


Fig. 2.

The heat of solution is here thermochemically positive; and zero in  $F$  and  $C$ . The explanation is now as follows:

The dissolution of the solid substance  $a$  considered by itself will be accompanied by absorption of heat; the formation of the compound, this being exothermic, with development of heat. In that region of temperature in which the formation of the compound chiefly takes place, it may, therefore, happen that the heat of formation of the compound exceeds that which is absorbed during the dissolution. This is the case from  $F$  to  $C$ , between which temperatures, as seen in the triangle, the dissociation isotherms are the most divergent and the quantity of the compound formed, therefore, increases most rapidly with a decreasing temperature.

The solubility-isotherms for  $a_2$  will, at a sufficiently low temperature, approach to the side  $b_2 ab$ . If at a lower temperature the combination is complete, the intersection of the dissociation- and melting-isotherm will finally come very close to the angular point of the compound and the projected melting point line will, therefore, become an asymptote to the straight line  $PQ$  which indicates the composition of the compound. It is also possible that the melting point curve does not intersect the straight line  $PQ$  for the second time but remains to the right of  $PQ$ .

When a larger quantity of the compound is already present at a higher temperature, the bend is shifted further to the left, so that it may happen that the melting point line is not intersected by  $PQ$ .

If the formation of the compound takes place over a larger temperature interval, the bend  $BCDF$  may disappear from the line and there may only remain a more strongly inclined part.

In a similar manner the solubility line for the compound  $ab$  or for the component  $b_2$  may be determined. The different forms which these lines assume either wholly or in those parts which, owing to their mutual interference, are alone capable of existence, are again entirely dependent on the manner in which the solution-isotherms shift in regard to the dissociation-isotherms.

In this way all the known cases of the meeting of the lines of the components with those of the compound may be deduced. It also is shown how it is possible that the compound which exists partly in the liquid *cannot* separate in the solid condition and must, therefore, again be decomposed when the components solidify.

Another case, as yet unknown, may also be possible namely that after the solidification of the two components by *cooling* a liquid is again formed from which on further cooling the compound is depo-

sited (Fig. 3). This case is possible when the lines of the components have the shape of Fig. 2 and meet above  $C$ .

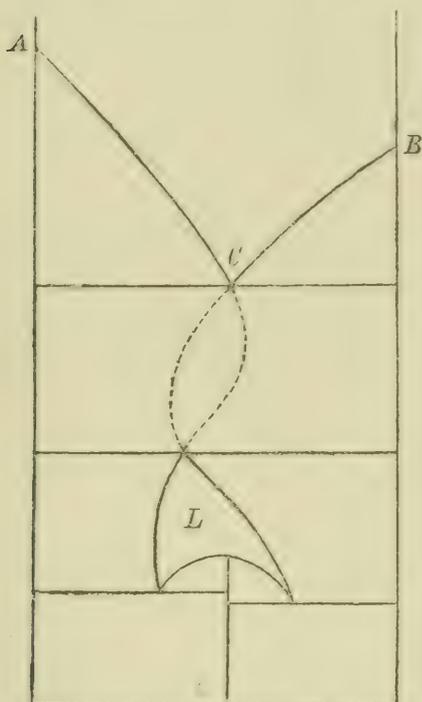


Fig. 3.

curve with two vertical lines in points where the heat of solution is zero, and two melting points.

In the space indicated by  $L$  there exist again unsaturated solutions all situated below the eutectic point  $C$  of  $a + b$ .

When the compound is endothermic the order of the dissociation isotherms is the reverse of that indicated in Fig. 2. Without entering into all the peculiarities which the solubility-lines may then exhibit, attention must be called to two as yet quite unknown types of melting point lines which may occur (Figs. 4 and 5).

In the first figure we have the remarkable fact that the compound forms with the component  $a$  a eutectic point  $C$  as well as a transition point  $D$ . In the second figure, the melting point line of the compound occurs as a closed curve with two vertical lines in points where the heat of solution is zero, and two melting points.

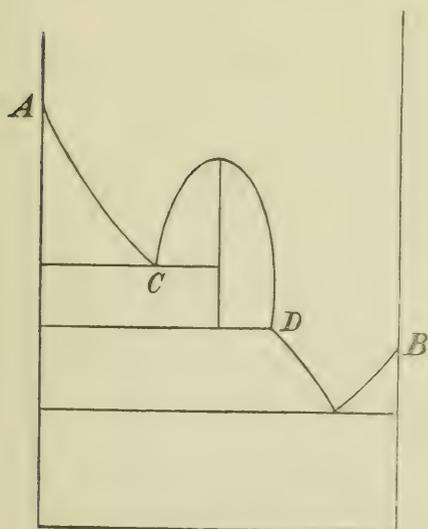


Fig. 4

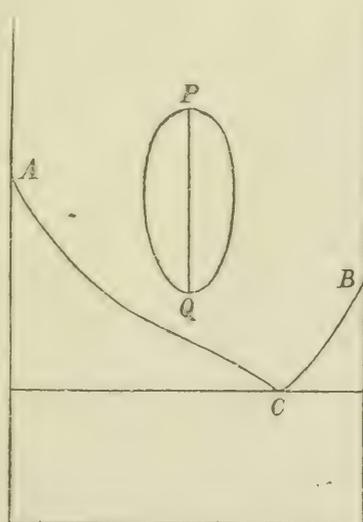


Fig. 5.

In the upper point *P* the compound passes into the liquid state, heat being absorbed. This absorption consists of two parts, the ordinary heat of fusion and the heat evolved when a part of the liquid (endothermic) compound decomposes until the equilibrium in the liquid is reached. As at higher temperatures the quantity of the compound in the liquid is large, the second quantity of heat will be small in comparison with the first and the melting will cause absorption of heat.

At *Q* it is, however, just the reverse because at a low temperature there exists but little compound in the liquid and the dissociation of a large proportion of the liquid compound may evolve so much heat that this exceeds the actual heat of fusion of the solid compound. The total fusion therefore produces heat and consequently the liquid field is situated below *Q*.

Up to the present, however, no endothermic compounds are known in the liquid state.

**Microbiology.** — Professor BEJERINCK presents a paper from himself and Mr. A. VAN DELDEN: “*On the bacteria which are active in flax-rotting*”.

(Communicated in the meeting of December 19, 1903).

### 1. *How far flax-rotting should go.*

The object of flax-rotting is the partly solving and softening of the rind of the flax-stalk to remove the *pectose*, in consequence of which the bast-bundles are freed so that later, after drying, the fibres may easily be separated from the wood by breaking and scutching. Pectose (*pt* Fig. 1) is the substance of which the young cell-walls consist, as also the outer layers of the old cell-walls; these walls are further built up from *cellulose*, which in a good rotting does not undergo any change<sup>1)</sup>.

By the rotting also the middle-lamellae, by which the fibres in the bast-bundles stick together, may go into solution and consequently the bast-bundles would be decomposed into the fibres proper. This is not desirable as in this case no large coherent “lints” would be got in scutching, but only loose fibres, of about 2 cm. in length.

The fibres of the bast-bundles, however, separate with much greater

<sup>1)</sup> For the microbes which affect the cellulose proper see OMELJANSKY, *Centralb. f. Bacteriol.* 2 Abt. Bd. 8 p. 193, 1901, and G. VAN ITERSON. *These Proceedings* 24 April 1903.

difficulty than the cells of the rind, because, in the middle-lamellae between the flax-fibres, besides *pectose*, also *lignose* is found<sup>1)</sup>, which is not affected by the rotting (*ly* Fig. 1).

It is just by the absence of lignose that the rind is so much more easily affected by the rotting process than the bast-bundles, that the latter, in a well-conducted rotting keep together and may be obtained after the scutching as a whole.

Hence, the art of rotting consists in pushing the process on to a determined point and no further.

It is not easy to indicate where this point is situated, chiefly because the flax-stalks, which at the pulling from the field are united into sheaves for the rotting, are not all equally ripe. As now the unripe stalks are more easily rotted than the riper and tougher ones, a very unequal product is obtained by submitting all to a like process. Therefore great pains are taken at the Leie, near Courtray, as much as possible to sort the flax before the rotting, in order to form lots of the same quality. Moreover, they rot the flax there twice, which renders it possible partly to redress the irregularities originated in the first rotting.

From a theoretical point of view we assume that rotting should proceed just so far ("strong rotting") as is necessary for the easy removing of the wood (*xy* Fig. 1) from the bast-bundles (*f* Fig. 1), but not so far ("feeble rotting") as to decompose them into the elementary fibres. Therefore it is necessary that the secondary bark (*cs* Fig. 1) of the flax-stalks be quite dissolved and that the primary rind (*cp* Fig. 1) be decomposed into cells<sup>2)</sup>.

## 2. *Pectose and Pectine.*

Pectose is a lime compound whose composition is not yet clear. Non-reckoning its rate of lime, this substance, though chemically related to, is not identic with cellulose. According to TOLLENS and TROMP DE HAAS<sup>3)</sup> we find for it, after removing the lime, the

1) J. BEHRENS, *Natürliche Röstmethoden. Das Wesen des Röstprocesses vom chemischen Standpunkte. Centralbl. f. Bacteriologie, 2te Abt. Bd. 8, pag. 161, 1902.*

2) Whether this standpoint is right in all cases (or rather will prove to be so when the flax industry will have ceased to be a very primitive agricultural industry) is doubtful. As in a good rotting process the flax-fibre itself is not injured, it is an open question whether the spinner might not be able to spin threads of greater equality from the wholly isolated fibres, then when they are still united in bast-bundles of very unequal properties.

3) *Untersuchungen über die Pectinstoffe, LIEBIG's Annalen der Chemie. Bd. 286 p. 278, 1895 and TOLLENS, Ueber die Constitution des Pectins. Ibid. p. 292.* As in hydrolysis the pectinic substances, besides glucose and galactose, also yield pentose, TOLLENS gives as probable composition  $(C^5 H^5 O^4)^{11}$ .  $C^5 H^5 O^5$ .

formula  $n(C^6 H^{10} O^5)$  or  $n(C^{12} H^{22} O^{11})$ , but not exactly, a small excess of O pointing to the presence of a COOH-group, which should be substituted in the pectose (the said authors use the word pectine). TOLLENS takes the here concerned acid for gluconic acid ( $C^6 H^{12} O^7$ ), or an acid related to it, and this would occur in the pectose as lakton or ester, that is in neutral condition. He calls pectose an oxy-plantslime, but does not mention the lime.

By treating with acids the various pectose-forms are more or less

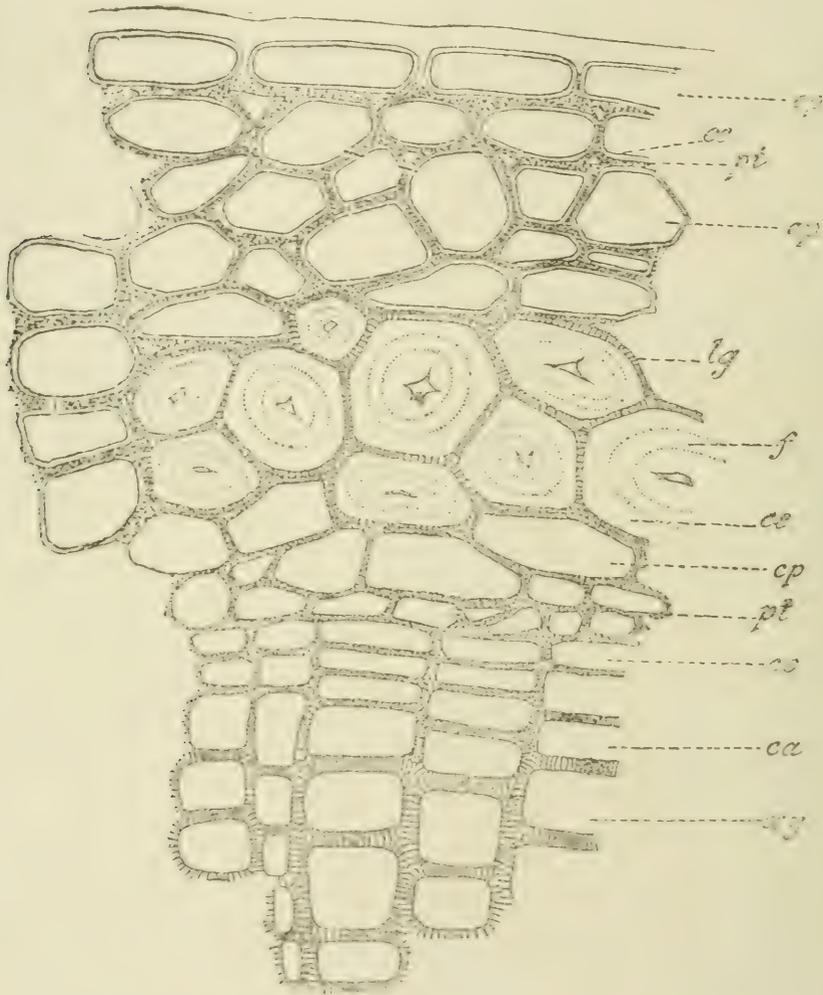


Fig. 1 (550). Transverse section of the bark and wood of a flax-stalk, *Pectose* *pt* dotted, *cellulose* *ce* left white, *lignose* *lg* hatched lines; *ep* epidermis, *cp* primary rind-cells with outer wall of pectose, *f* bast-fibres with outer wall of pectose + lignose, *cs* secondary rind cells, and *ca* cambium-cells whose walls quite consist of pectose, *xy* wood, with large punctations.

easily hydrolysed, the pectose of the flax not so easily. Hereby first result pectine or metapectine, which have an acid character and are therefore also called pectinic acid and metapectinic acid. The pectine gelatinises in presence of lime, through the enzyme pectase, moreover through alkalies and ammonia, likewise in presence of a lime salt.

In absence of lime the compounds of alkalies with the pectine are soluble in water. Gelatinisation proper is unknown with metapectinic acid.

With continued hydrolysis, pectine and metapectine, hence, also pectose, produce galactose and pentose, and according to TOLLENS, with certain pectine kinds, dextrose and arabinose too, which sugars are easily fermented by *Granulobacter*.

By boiling with nitric acid pectose and pectine yield mucous acid.

Pectose is insoluble in cold and boiling water and in cupri-oxylde-ammonia. The pectose of the flax-stalk is moreover not easily affected by dilute acids and alkalies, and remains unchanged after a short heating in water-vapour at 120° C.

Pectose can be softened by the successive influence first of an acid then of an alkali. If the flax-stalk is first extracted with dilute hydrochloric acid, by which the pectose changes into pectine, which however, as an insoluble lamella, still holds the cells together, washed out to remove the lime, salts become soluble by the hydrochloric acid, then treated with ammonia or natriumcarbonate, a considerable softening takes place. On this method, first suggested by MANGIN<sup>1)</sup>, repose the so-called chemical rotting after the patent of BAUER, which has, however, produced nothing of practical use, and only shows that the "inventor" did not know the requirements to which well-rotted flax should answer.

A better way of dissolving the pectose of the flax-stalks we found by placing them in a strong solution of ammonium-oxalate, but only after 3 weeks the rotting process was completely finished, so that this means has not any practical value either.

Whereas the preparation of pure pectose is troublesome in consequence of its insolubility, it is easy to make pectine.

Herefor<sup>2)</sup> one takes the rootstocks of *Gentiana lutea* of the chemists, grounds them finely, first extracts with H<sup>2</sup>O and places

1) Although it may be read everywhere that pectose after MANGIN's method goes "into solution", it is my experience that this is exaggeration, and that, of the decomposition of parts of plants into free cells as in rotting, there is no question in this case.

2) To compare BOURQUELOT and HÉRISSEY, Journal de Pharmacie et de Chimie, Sér. 6, T. 8 p. 145, 1898.

the washed material under a large quantity of 3% HCl, filtrates, and precipitates with alcohol. The precipitate is dissolved in boiling water, precipitated again with alcohol and this is repeated until the chlorine reaction disappears. The thus obtained pectine reacts feebly acid and solidifies with pectase + a lime salt, or with alkali + a lime salt, into a consistent transparent jelly.

3. *The rotting is caused by microbes and may be called pectose-fermentation.*

Dissolving and removing of the pectose from the rind of the flax is completely effected, without any injury of the cellulose wall of the *fibrés*<sup>1)</sup>, by some microbe species belonging to the moulds and bacteria, and hereupon the usual rotting methods are based.

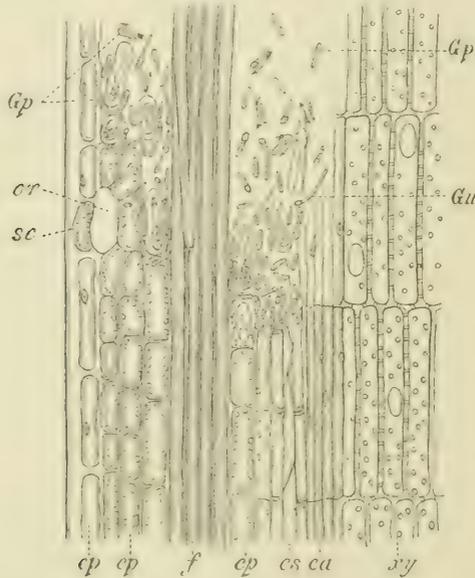


Fig. 2 (350). Rotting observed in a microscopic preparation lying in a drop of good rottingwater and consisting of a longitudinal section of the rind and the wood of a flax-stalk. Signification of the letters see Fig. 1, further: *sc* cell of a stoma, *or* air chamber in the primary rind, *Gp* *Granulobacter pectinovorum*, the pectose bacterium proper, *Gu* *Granulobacter urocephalum*. The primary rind *cp* is seen to decompose into cells by solution of the pectose, and thereby the secondary rind *cs* and the cambium *ca* completely liquefy.

Moulds are the active agents in the very primitive so-called dew-rotting on the field; bacteria on the other hand, in the rotting after

<sup>1)</sup> But not of the cellwalls of the rind-cells from which the cellulose itself is also partly dissolved.

steeping of the flax in water, that is in the white- and the blue-rotting.

In the dew-rotting a most unequal product is obtained; this process shall not further be discussed here.

In the blue-rotting in ditches and ponds, as also in the white-rotting, a so-called anaerobic bacterium is the active agent. This highly interesting organism belongs to the genus *Granulobacter* and shall be called *G. pectinovorum*<sup>1)</sup> (*Gp* fig. 2). At the present moment the whole rotting industry is nothing else but a more or less rational culture-method of this bacterium.

From a theoretical point of view it is interesting that there are also some aerobic bacteria with which rotting is possible with free access of air. These are the various kinds of the so-called hay-bacteria group, also known by the name of potato-bacteria, the chief species of which are *Bacillus mesentericus vulgatus*, *B. subtilis*, and *Granulobacter (Bacillus) polymyxa* (= *B. solaniperda* KRAMER).

#### 4. *Arrangement of the rotting experiments in the laboratory for the examination of microbes in pure culture on their power of rotting.*

In order to ascertain if any microbe can be used for rotting it is necessary to dispose of perfectly sterile flax. This is obtained by heating the flax for some time at 125—130° C. in the steam sterilisator, whereby it is seen that it is not rotted at all by this overheating.

For the laboratory experiments with the "anaerobes", thick walled test-tubes were so closely filled with flax, washed out or not, that the pressure against the glass-wall prevents it from mounting up when the tube is further filled with water. After cotton-plugging the filled tubes are sterilised in the sterilisator.

It is true that in these tubes air can penetrate from above, but if the pieces of the flax-stalks are not too short, say 20 cm., the entrance of air is not noxious to the anaerobes, provided some ordinary aerobic microbe be added, which lives at the surface and there absorbs the oxygen. We always used to this end a *Torula* yeast.

For testing the aerobic microbes the flax is spread in a thin layer at the bottom of a wide ERLIENMEIJER-flask, and after immersing in a little water the whole is sterilised, after cooling infected with the species concerned and cultivated at 35°, or lower, in accordance with the microbes to be examined. After 2 or 3 days the rotting is finished.

<sup>1)</sup> First discovered by WINOGRADSKY (*Comptes rendus* T. 121, pag. 742, 1895). STÖRMER (*Mittheil. der deutschen Landwirtschafts Gesellschaft* Bd. 32, pag. 193 1903) used for it the name of *Plectridium pectinovorum*.

At the examination of the numerous microbes which may be obtained from flax in rotting condition, the result was negative for by far the greater part of the species. No rotting was to be observed with the various kinds of yeast, of *Mycoderma*, of *Torula*, of *Oidium* and of red yeast, nor with the lactic-acid ferments, the vinegar bacteria and the different forms of the *Aerobacter*-group, such as *A. coli* and *A. aerogenes*, which organisms are all universally found in the rotting water of natural rottings.

The aerobic bacteria of the hay-bacteriagroup (*B. mesentericus* and *B. subtilis*), which, at sufficient supply of air are on the contrary strong rotting-organisms, are rare in good rotting water. For rotting they should be kept at least at 30°.

5. *The rotting reposes on the action of the enzyme pectosinase which is secreted by the pectose-bacteria.*

The action on the flax, as well of the anaerobic *Granulobacter pectinovorum* as of the aerobic hay-bacteria and the moulds, is caused by a specific enzyme *pectosinase*<sup>1)</sup>. This enzyme, like the acids, exerts an hydrolytic influence, first converts the pectose into pectine, and subsequently the pectine into sugars, which are fermented by *G. pectinovorum* (*Gp* fig. 2) under production of hydrogen, carbonic acid and a little butyric acid, and assimilated in case the hay-bacteria are used for the experiment.

These sugars are most probably galactose and xylose, and (perhaps in some cases) also glucose and arabinose, which as we saw before, have been found by TOLLENS as products of the hydrolysis of the pectinic substances with acids.

Pectosinase is not easily soluble in water and can be precipitated with alcohol. In presence of chloroform and in absence of the microbes, we succeeded thereby to decompose into cells thin slices of potato, and further to liquefy with it solid plates of pectine, made by solidifying pectine from *Gentiana lutea* (see § 2) with pectase + CaCl<sup>2</sup>. The action of the isolated enzyme is feeble, much feebler than when also the secreting bacteria themselves are present in living condition. This is evident from the facility with which the hay-bacteria at 37° C. decompose slices of living potatoes, whilst this gives much more trouble when effected by the enzyme prepared separately.

<sup>1)</sup> Not identic with the "pektinase" of BOURQUELOT and HÉRISSEY (Comptes rendus T. 127 pg. 191 1898) from green malt (which is identic with the "cytase" of BROWN and MORRIS (Journ. Chem. Soc. Trans. 1890, p. 458)) for with malt flax cannot be rotted.

The insolubility of pectosinase in water and, much more the fact that all the pectose bacteria examined by us lose suddenly in certain not well defined circumstances the power to secrete it render the study of this enzyme very troublesome. Particularly important is its following property.

*Whilst the action of the pectosinase is favoured by a little acid, the growth of the pectose bacterium is retarded by acid.*

As to the rotting-process, for which the *production* of the enzyme is clearly the essential point, one has, if not exclusively, at least chiefly to reckon with the properties of the microbes themselves, more especially with the conditions for *their production*. Hence, from this point of view only a slight production of acid will be favorable for the rotting.

From the above it follows that the chief question of flax-rotting is: what are the conditions of life of the bacteria concerned and how can their multiplication and accumulation in the flax-stalks be attained so profusely as to expel the other microbes, and, by a sufficient formation of pectosinase cause the rotting-process to go on regularly?

WINOGRADSKY has, it is true, partly answered this question by the discovery of the pectose-bacterium. But the essential point in the arrangement of a rotting experiment has quite escaped him, for he has not recognised the necessity of the water refreshing. Hence, hitherto there exists no clear method which may give rise to a natural accumulation of the bacteria specifically concerned in the rotting and accordingly neither for the really rational arrangement of the rotting-process.

This gap will be filled-up here.

#### 6. *Fundamental experiment for the explanation of the rotting-process.*

A cylindrical glass vessel *A*, Fig. 3 is quite filled with flax *V*, so that the stalks by their pressure mutually and against the glass-wall, are prevented from floating up as the vessel is further filled with water. Thereby is obtained 5 to 10 % of weight in flax to 100 of water.

To the bottom of the vessel *A*, a glass tube *B* reaches, through which pure water can flow down from the higher placed reservoir *C*. This water flows upward through the flax-stalks, according as the washing-water flows off by the tube *D*, and thereby extracts most of the soluble substances from the flax, whilst the insoluble

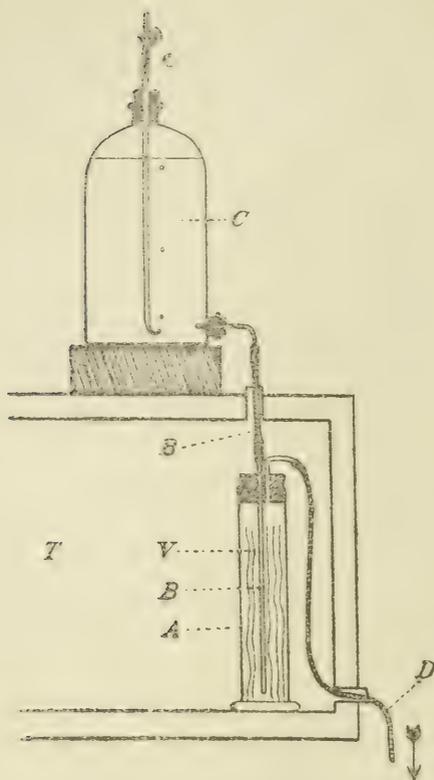


Fig. 3. Apparatus for rotting-experiment with water-current. *A* cylindrical glass jar with flax *V*, *B* tube supplying water from the reservoir *C* to the bottom of *A*, *D* tube to draw off the water. *T* thermostat.

pectose remains behind in the stalks. What is drawn off by *D* may be called "rotting-water", but this water is widely different, at the starting of the experiment, when it contains much dissolved matter and few bacteria, from that, obtained in a later period, when many bacteria and few dissolved substances occur in it.

The jar *A* is kept at a temperature of 28 to 35° C. by placing it in the thermostat *T*.

If after 2 or 3 days the flax is removed from *A* it proves to be more or less sufficiently rotted, if the water supply has been great enough to refresh the rotting-water from 5 to 10 times. Through our apparatus of 300 cc., 1.5 to 3 l. of water had thus to pass. Whilst in the Laboratory experiment the water is introduced at the bottom of the jar and drawn off at the top in order to prevent stopping of the tubes by the gases formed by the fermentation, this would be faulty with experiments on a larger scale, — in this latter case the heavier rotting-water should be drained off at the bottom.

If the rotted bark of the flax, or the pith, or the juice, contained in the rotted stalk, is microscopically examined, we find there accumulated the above mentioned very characteristic *Granulobacter pectinovorum* (Plate Fig. 1), which has supplanted nearly all other microbes and which literally fills up the intercellular spaces (*G.* Fig. 2), in many places quite covers the surface of the fibres and has, moreover, completely dissolved the thin-walled cells of the secondary rind, and thereby freed the bast-bundles from the wood. In an iodine solution this bacterium turns deep blue over nearly its whole length in consequence of its amount of granulose.

This is a so-called anaerobe. From the experiment described, where an aerated water-current incessantly flows around the flax, it follows, however, that a fair amount of air is of no prejudice to its development; and a more minute observation shows that here, too, as with all other anaerobes, a limited aeration is not only harmless, but beneficent, and even necessary to make the growth go on in the long run.

Our observation that the water of the Leie, near and at Courtray, is strongly polluted by sulphuretted hydrogen, induced us to add c. a. 50 mgrs. of  $H^2S$  per l. to the water for our rotting-experiment, by which even in the rotting-water flowing off a little  $H^2S$  might be detected. The rotting was decidedly retarded by this addition and was less complete than in absence of sulphuretted hydrogen; yet, *G. pectinovorum* had strongly accumulated, though less profusely than commonly.

Quite otherwise was the effect of  $KNO^3$ . If 0.2 grs. of it were added per l. of the water-current, then a trace of  $KNO^3$  might still be demonstrated in the rotting-water. Accumulation of *G. pectinovorum* and rotting proved complete in this case, so that, when Mr. PLAISIER, flax-merchant at Hendrik Ido Ambacht, came to judge of our rotted flax-samples, he classified our saltpeter-flax as "first rate". But it is clear that the presence of saltpeter is not necessary.

In fact, the accumulation of bacteria in the said experiment reposes, besides on the slight but necessary aeration, on the circumstance that by the water-current in the first 24 hours, such a complete extraction of the flax is attained, that all soluble nitrogen compounds are nearly completely expelled from it, and only the not easily soluble protoplasmatic proteid remains in the flax-cells, which substance, together with the still present carbohydrates and the pectose, prove to be the very nutriment for *G. pectinovorum* and, moreover, the food required to give rise to the secretion of pectosinase, hence, to the rotting-process. If the extraction has not taken place and the

experiment is made without the water-current going through the flax, a rich growth of all kinds of other bacteria will arise, but a real accumulation of *G. pectinovorum* and a good rotting-process is not obtained in the first two or three days.

The cause of this striking phenomenon reposes exclusively on the competition of the different microbe species. This is evident from the fact that with pure cultures of *G. pectinovorum*, even without refreshing the water, a very good rotting is possible. The substances removed from the flax by the water-current are not in themselves prejudicial to *G. pectinovorum*, but they favour the growth of the other species, in particular of the lactic-acid micrococci, so much more strongly, that *G. pectinovorum* can develop only later and with very great difficulty. It is also certain that the secretion of pectosinase in the dilute liquid is more profuse than in the more concentrated nutrient solutions. Thus we did not succeed in rotting flax by placing it in dilute sterilised malt-extract with chalk, of about 2° on the saccharometer of BALLING, which was in a vigorous fermentation by a pure culture of *G. pectinovorum*. Evidently no pectosinase secretion takes place under so favourable nutrient conditions.

Hence, there is a double reason why extraction so much promotes the rotting: the pectose bacterium gets the ascendancy, and its faculty of secreting pectosinase becomes active.

If we compare the microscopic image of the bacteria (Pl. Fig. 1) of the flax, rotted after the current "experiment", with that, treated in the usual way, after the white or blue rotting methods, one is struck by the enormous difference. In the latter case hardly anything is seen but the foreign species and *G. pectinovorum* is scarcely detected; whilst in the product, obtained by the current-experiment *G. pectinovorum* is seemingly in pure culture<sup>1)</sup>.

#### 7. Simplification of the current-experiment.

When the great importance for the rotting-process of extraction of the flax-stalks and of aeration had been recognised, it was natural to try whether the current-method could be replaced by a more rational way of water-refreshing for the practice.

This was effected in the following simple manner.

After standing 24 hours on the flax, the water was completely decanted off, so that all spaces between the stalks were drained and could fill with air. Subsequently a new supply of water was provided, either of fresh water of about 30° C. or of good rotting-water of

<sup>1)</sup> Compare further § 12.

a previous rotting. When using fresh water it proved desirable after every 24 hours to repeat the refreshing, but when good rotting-water could be had a second renewing was not required, good rotting-water containing already a sufficient accumulation of *G. pectinovorum*.

By this treatment, too, which may be called the "decanting method", excellent rotted samples were produced in 2½ or 3 days. It even seems that it should be preferred to the "current method", because by decanting the concentrated rotting-water will be enabled more completely to flow off from the narrow interspaces of the flax-stalks than will be possible when replacing it by slowly streaming pure water. For the same reason the *aeration* must needs be more complete anywhere in the sheaves by "decanting" than by "streaming."

On account of these experiences there is no doubt but any other method of water supply which can give rise to a sufficient extraction and aeration, can replace the "streaming" and the "decanting method", if only care be taken during the rotting not to injure the delicate and easily bruised flax-stalks.

Here once more it may be observed, that although *G. pectinovorum* belongs to the so-called obligative anaerobic bacteria, the strong aeration, described above, should be pronounced decidedly favorable to this bacterium. This is, however, quite in accordance with the experience acquired for all other well-observed anaerobes. Hence, it may be considered as a truth, confirmed by each subsequent research, that anaerobes, in the strict sense of the word, do not exist, and that the term "microaerophily" more precisely denotes the relation between such organisms and free oxygen, than the term "anaerobes".

#### 8. *Application of the current experiment for practical rotting* <sup>1)</sup>.

Practical rotting has until now been managed in a very primitive way. Even at the Leie, near Courtray, from whence the best flax-fibre comes to the market, even the superficial observer is struck by the numerous and great deficiencies existing there.

<sup>1)</sup> By "vat-rotting", the bleaching of the flax on the field through light, so essential in "white rotting", is excluded. In the flax-rotting establishments to come, it will therefore be necessary to make the rotting be followed by a chemical bleaching process. Experiments have shown that ozon or hydrogen-superoxide may be used to this end. Whether hypochlorites ("electrical bleaching") will also prove applicable without weakening the fibres, will have to be made out by dynamometrical estimations. Vat-rotting will also call attention to good drying-apparatus and, no doubt, to other troublesome problems, which, completely to solve, will require surely much time and many an industrial effort.

The first step towards improvement was taken in our country already in 1892 by the Society for the Promotion of Flax-Industry, which tried to replace the rotting in open water by rotting in vats.

After this method the flax-sheaves are placed vertically and close to one another in a large wooden trough, in which, at some distance from the bottom, a second, perforated bottom is fitted. This false bottom supports the flax and underneath the heavier rotting-water is collected, which flows down from the flax after the vat has been quite filled with water.

Baron RENGERS at Oenkerk, too, has tried to improve the rotting of flax, by treating it after the so-called hot-waterprocess, by which he seems to have obtained very satisfactory results.

Vat-rotting and hot-waterrotting can, however, only succeed with sufficient certainty, when care is taken to provide a due refreshing of water; this may be done in various ways, but has not hitherto been sufficiently attended to.

By "vat-rotting" the following advantages may be obtained.

*First.* The vats can be placed in a manufactory, where the other manipulations which the flax has to undergo, can also be effected.

*Second.* The temperature of the rotting-water may be modified at will, by which the difference between vat-rotting and hot-water rotting disappears. Rotting will be possible throughout the year.

*Third.* The extraction and aeration of the flax can easily be regulated, so that the accumulation and multiplication of the pectose bacterium is made sure, and the lactic-acid micrococci, the great enemies in the rotting process, are expelled.

The theoretical requirements for vat-rotting are in general to be seen from what precedes, but it is still necessary to call attention to the following points on which the success of that process depends.

In the first place, care should be taken that the heavier water, produced by the extraction of the flax, can easily be removed. By the use of a false bottom the water collects underneath the flax, so that it is possible first quite to fill the vat, allow it to stand for 24 hours, and then to drain off all the water. The flax thereby comes quite equally into contact with the air, so that even the densest places of the sheaves are duly aerated ("decanting method").

It will be sufficient only once to refresh the water<sup>1)</sup>.

<sup>1)</sup> The experiments with pure cultures of the pectose bacterium prove that theoretically the refreshing of the water is not even once fully required, but probably the competition, particularly of the lactic-acid and butyric-acid ferments, struggling to displace the pectose bacterium, will render this ideal condition unattainable for vat-rotting on a large scale.

It is a mistake to draw off the rotting-water from the vats at the top and introduce the fresh water at the bottom. Hereby the heavier washing-water is driven back among the flax-stalks and renders a complete extraction impossible, because the rising water will always seek those places, where there is the least resistance, i. e. the open-spaces of the sheaves, and will not enter the close places, where it is most wanted. Thus the growth of the pectosebacterium is hindered and that of the lactic-acid ferments promoted. Moreover the aeration, which, when the washing water is completely drained off, takes place of itself, and quite equally and everywhere throughout the flax, would become most irregular and imperfect.

In the second place, the vat should after the first draining not be filled with fresh water only, but this water should be mixed with a fair quantity of *good* rotting-water, taken from a previous rotting. By this means the pectose bacteria are at every point introduced into the flax, which of itself harbours only a small number of these microbes, which are not at all generally distributed, neither on the flax nor in the waters.

Before commanding of good rotting-water it will be necessary once more after 24 hours, so two days after the first filling, to draw off all the water and replace it by fresh water. The pectose, bacteria have then already so strongly accumulated in the flax-stalk, that they can only for a small portion be washed away.

How easily *good* rotting-water is to be obtained follows from the description of the current-experiment.

In the third place the rotting-temperature will have to be exactly regulated. Our laboratory experiments make it evident that the most favorable temperature lies between 28° and 35° C. After 2½ to 3 days the flax may then be removed from the vats in an excellent rotted condition (see note 1 § 8). Perhaps with a longer rotting-time the temperature might be lowered and reduced to from 25° to 27° C. Practice will have to decide whether this is desirable.

### 9. *Pure culture of the pectose bacterium.*

The pure culture of *G. pectinovorum*, which like all other species of *Granulobacter*, produces spores, is successfully effected as follows.

On a culture medium in a glass box, consisting of dilute malt extract of c.a. 2% BALLING, with 2% agar and 2% chalk, some material taken from the rind of a well-rotted flax-stalk, pasteurised at 90° C., is put, in order to obtain colonies of *G. pectinovorum* in streak-culture. The pasteurisation serves to kill the foreign

bacteria of which the majority produce no spores, in particular the lactic-acid ferments, but it should not be done at too high a temperature, as also most spores of the pectose-bacterium itself die already at the boiling point.

The glass-box is now placed in a well-closing exsiccator, with a three way stop-cock, in which a small dish with hydrosulphite of sodium is put. The exsiccator is evacuated by a KÖRTING pump, filled with hydrogen (or carbonic acid), and again evacuated; and this is repeated until it may be assumed that the oxygen, which can never be completely removed, is reduced to the minimum pressure tolerated by the anaerobes, wherein the hydrosulphite is also useful. The exsiccator is placed in a thermostat at about 35° C. and after 2 to 3 days the anaerobic colonies are seen to develop. They chiefly belong to the four following species of *Granulobacter*:

1. *G. pectinovorum*.
2. *G. urocephalum*.
3. *G. saccharobutyricum*.
4. *G. butylicum*.

The third of which was alluded to and the fourth described by me in a former research<sup>1)</sup>. The two first species only, viz. *G. pectinovorum* and *G. urocephalum*, are real rotting-bacteria, the former acts strongly, the latter feebly rotting. The two last mentioned, viz. the butyric acid ferment (*G. saccharobutyricum*) and the butylic ferment (*G. butylicum*) cause no rotting at all.

The colonies of all the four kinds colour deep blue when treated with iodine solution, in consequence of their contents of granulose in thin, elongated clostridia. Besides, rodlets are found in all colonies, which do not stain blue with iodine, and which, in a former paper, have been described as "oxygen forms" of *Granulobacter*<sup>2)</sup>. Some colonies consist of the oxygen form only, hence do not stain with iodine at all, and only contain rodlets, in which spores are seldom found.

If the material taken from the flax-stalks has not been sterilised previously to the sowing, various colonies of lactic-acid micrococci will develop on the plates, surpassing the *Granulobacter* colonies many times in dimensions and thereby easily recognisable.

#### 10. Description of *Granulobacter pectinovorum*.

The colonies of this bacterium are recognised by the "moiré-phenomenon", figured on Plate Fig. 3. It consists in the appearance

<sup>1)</sup> Sur la fermentation et le ferment butyliques. Archives Néerl. T. 29, pg. 1. 1896

<sup>2)</sup> Fermentation butylique. pag. 35.

of characteristic, nearly rectangular dark and light fields to be observed in the colonies when obliquely illuminated, which fields can interchange of tint and originate by the reflexion of light on groups of mutually parallel bacteria; of the different groups the longitudinal axes meet at nearly right angles.

As to the bacterium itself, its description by WINOGRADSKY<sup>1)</sup> is in good accordance with our results. It is a rather long species, producing spores at a terminal swelling (a little beneath the end) of the very long and very thin clostridia, resembling common staves, which then look like frog-spawn (Plate Fig. 4). The rodlets are 10 to 15  $\mu$  long by 0.8  $\mu$  wide but eventually much longer. The older ones become thicker and swell at the end, to 3  $\mu$  in width; the oval spore, formed in this swelling, measures 1.8  $\mu$  by 1.2  $\mu$ .

In dilute malt-extract, with exclusion of air, a vigorous fermentation takes rise, without formation of butyric acid.

With starch<sup>2)</sup>, inulin, mannite, erythrite, glycerin, fermentation could not be produced under any circumstances.

With peptone and with dilute broth, or albumine as sources of nitrogen, our bacterium causes fermentation in glucose, laevulose, galactose, milksugar, and maltose, with a slight production of butyric acid. Proteids and gelatin are peptonised.

With ammonium salts as source of nitrogen, fermentation cannot be produced with any of these sugars. Nitrates are not assimilated and not changed at all.

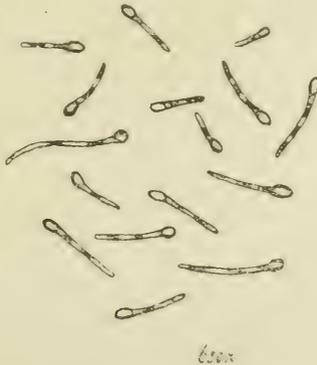


Fig. 4 (650). Culture of *Granulobacter pectinovorum* in pectin-ammonium-sulphate solution. The thick ends contain oval spores; the dark spots in the rodlets indicate granulose.

<sup>1)</sup> Comptes rendus T. 121, p. 744, 1895.

<sup>2)</sup> WINOGRADSKY asserts that starch does ferment.

Pectine, prepared as indicated § 2, is decomposed, as well with albumine, peptone, or broth, as with ammoniumsalts for source of nitrogen, by which this bacterium stands by itself and is sharply distinguished, especially from the butyric-acid and the butylic ferments, which do not attack pectine at all. When the pectose is attacked, pectosinase secretion occurs.

Cellulose as filter-paper, is not in the least affected by *G. pectinovorum*. Hence, the flax-fibre as such remains quite unchanged in the rotting, but the less resistant forms of cellulose are solved quite as the pectose itself. Gum arabic remains intact. As is seen from the photogram (Plate Fig. 2), the image of the pure culture on malt-extract agar is quite different from that of the butyric-acid ferment, which latter forms thick clostridia.

This difference is not less clear in the culture liquids. Thus, in fig. 4 we see the form of the bacterium in a pectine fermentation at 35° C. in: Tap-water 100, Pectine 2,  $(\text{NH}^4)^2 \text{SO}^4$  0,05,  $\text{K}^2\text{HPO}^4$  0,05, Chalk 2.

The dark portions represent the places where granulose is accumulated. Clostridia of the common form are completely absent. The shape of our bacterium in this or such like culture liquids is characteristic, and is not found in any other species except *G. urocephalum*.

#### 11. Description of *Granulobacter urocephalum*.

The difference between *G. pectinovorum* (*Gp* F. 2, Plate Fig. 3) and *G. urocephalum* (*Gu* Fig. 2 Plate Fig. 4) which likewise, albeit in smaller number, accumulates in the rotting flax, consists first in the shape, which for the latter more approaches the "drumstick form", although the spores are not round, but oval, as Fig. 2 § 3 shows with great distinctness. Further, in the former secreting a much larger quantity of the rotting-enzyme pectosinase, which is the very reason why *G. pectinovorum* is more common in rotting flax than *G. urocephalum*.

Both species produce much mucus, which consists of the thickened and liquefied cell-walls of the bacteria themselves, and is found back in the so-called rotting-gum, obtained by evaporation to dryness of the rotting-water. That this species also stains deep blue with iodine is suggested by the generic name.

A characteristic difference between the two species is the following.

The colonies of *G. pectinovorum* (Pl. Fig. 3), when kept on plates of dilute malt extract agar with chalk, will relatively promptly be decomposed into a detritus, wherein only the spores can clearly be recognised, whereas the colonies of *G. urocephalum* (Pl. Fig. 4)

remain much longer unchanged and continue distinctly to show the shape of the bacteria. This phenomenon of bacteriolysis is perhaps associated with the pectosinase secretion and is also observed in the hay-bacteria.

The essential difference between *G. urocephalum* and *G. pectinovorum* is that the former with ammonium-salts as source of nitrogen, can ferment all kinds of carbohydrates, such as glucose, milk-sugar, cane-sugar and dextrine, for which *G. pectinovorum* requires peptone or broth. On the other hand, pectose is so little attacked by *G. urocephalum* that fermentation cannot be observed with this substance, even not when broth is present as source of nitrogen. Trypsin-formation is with *G. u.* about as vigorous as with *G. p.* and much more abundant than with *G. saccharobutyricum*. The secretion of diastase, on the other hand, is extremely feeble in both species and much less vigorous than in the butyric-acid ferment.

12. *Accumulation experiment for G. urocephalum. Why the butyric acid- and the lactic-acid ferments disappear from good flax-rottings.*

That *G. pectinovorum* so strongly accumulates in our "current-" and "decanting experiments", reposes on the double adaptation of this ferment, on the one hand to the insoluble albuminoids of the flax-stalk by a strongly peptonising enzyme, on the other hand to the insoluble pectose by the secretion of pectosinase.

Why *G. urocephalum* also accumulates in the flax, but much less strongly, and why the common and vigorous butyric-acid ferment disappears nearly completely, was made clear by the following accumulation-experiment for *G. urocephalum*, devised by Mr. G. VAN IJTERSON, at the occasion of a research on the butyric-acid fermentation.

If to any carbohydrate, for example insoluble starch, glucose, cane-sugar, or milk-sugar, a slight quantity of egg-albumine or peptone, or very little broth, is added as nitrogen source, in the proportion:

Tapwater 100, Glucose 5, Albumine 0.1,  $K^2HPO_4$  0.05, Chalk 5,

infected with garden-soil and cultivated in a stoppered bottle at 35° C., there will first, that is so long as soluble carbon compounds are still present, originate a butyric fermentation, but this is soon replaced by a *Urocephalum*-fermentation.

If from the thus obtained first fermentation a small drop is transported into the same mixture, the butyric-acid ferment, indeed, does not completely disappear, but the intensity of the *Urocephalum*-fermentation becomes thereby much enhanced. If at the end of the

fermentation a new quantity of sugar (and chalk) is added, a further purification of the ferment is observed.

When using a smaller dose of sugar, the soluble nitrogen compounds which occur in the albuminous matter, become more troublesome as they make the butyric fermentation more prominent.

If the same experiment is made, the albumine being replaced by an ammonium salt, *G. urocephalum* is quite expelled and the butyric ferment, *G. saccharobutyricum*, gains the victory.

That this experiment reposes only on competition, is proved by the fact that *G. urocephalum* in pure culture, can grow excellently and ferment with the said sugars and an ammoniumsalt as source of nitrogen. Further, the pure culture on dilute malt-extract gelatin proves that *G. urocephalum*, like *G. pectinovorum*, liquefies the gelatin much more strongly than the butyricferment, and thus secretes more trypsin.

The reason why these three bacteria accumulate so unequally in the flax in the "current-experiment", and why *G. urocephalum* takes the middle between the pectose-bacterium and the butyric ferment, is thus evidently as follows.

During the extraction the insoluble nitrogen compounds are removed, so that, as source of nitrogen there remains nothing else but the insoluble vegetal proteids. This assures the victory to the strongly peptonising *G. pectinovorum* and *G. urocephalum* over the not or feebly peptonising butyric ferment.

This latter yields much more diastase than *G. pectinovorum* and *G. urocephalum*, so that its presence is a source of sugar formation, starch being never completely absent.

Hence, as soon as the butyric-ferment disappears, the insoluble carbohydrates, too, will promptly be removed by the extraction and the fermentation. The insoluble pectose only is now left behind, by which *G. pectinovorum*, which secretes much pectosinase, finally also subdues *G. urocephalum*, which produces little or no pectosinase at all.

The lactic-acid micrococci produce no enzymes which attack proteids, pectose, or carbohydrates. So, from the moment, that only insoluble proteids and insoluble carbohydrates are present, they can no more multiply and are carried off by the water-current.

#### EXPLANATION OF THE PLATE.

Fig. 1 (600).

Drop pressed from flax-stalk at the maximum point of a rotting during the "current experiment", stained with iodine, and showing the natural accumulation

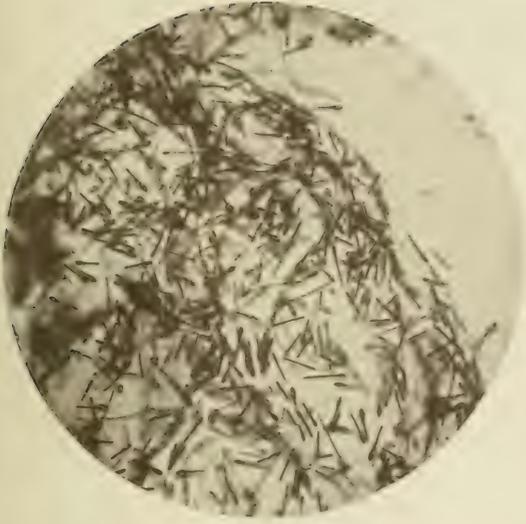


Fig. 1.



Fig. 2.

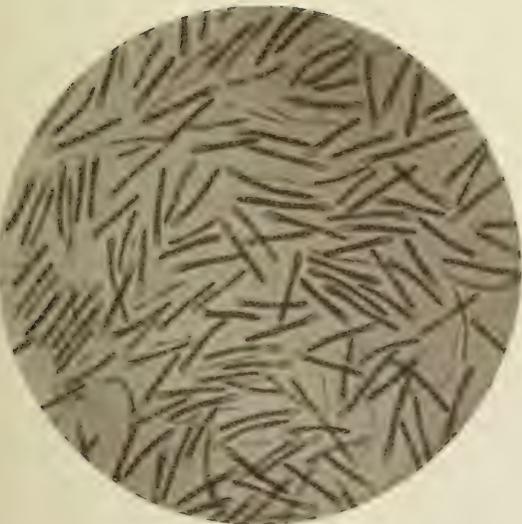


Fig. 4.

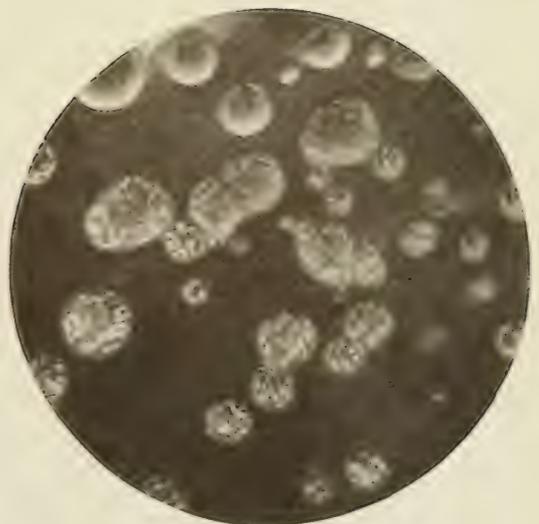


Fig. 3.



of *G. pectinovorum*, which is more, and of *Gr. urocephalum* which is less common. Here and there oxygen forms, which do not stain with iodine.

Fig. 2 (900).

*Granulobacter pectinovorum*, as pure culture, on dilute malt extract agar with chalk. Granulose stained blue with iodine, among the bacteria much detritus formed by bacteriolysis.

Fig. 3 (15).

Colonies of *G. pectinovorum* on the same culture medium to demonstrate the "moiré-phenomenon."

Fig. 4 (900).

*Granulobacter urocephalum*, as pure culture, on dilute malt-extract agar. No detritus is found among the bacteria.

**Physiology.** — "*On tactual after-images*". By Prof. J. K. A. WERTHEIM SALOMONSON. (Communicated by Prof. C. WINKLER).

(Communicated in the meeting of December 19, 1903).

In 1881 the following fact was mentioned by GOLDSCHIEDER in his thesis on "die Lehre von den specifischen Energien der Sinnesorgane":

"Wenn man mit einer Messerspitze schnell, am besten die Hohlhand berührt, so tritt momentan nur die Tastempfindung auf, welcher dann erst der stechende Schmerz folgt. Dasselbe kann man bei einem leichten Schlag mit der flachen Messerklinge wahrnehmen."

In the *Zeitschrift f. Klin. Mediz.* 1891 20. 4—6, he again takes up this subject in an article, signed likewise by Prof. GAD. This article has been republished afterwards in his *Gesammelte Abhandlungen* Bd. 2, pag. 376 under the title: "Ueber die Summation von Hautreizen".

In this article the conditions under which the phenomenon may be observed, are defined with greater accuracy. According to GOLDSCHIEDER the best result is obtained by exerting by means of the point of a pin a short and feeble pression on the skin of the back or of the palm of the hand: "so hat man ausser der ersten sofort eintretenden stechenden Empfindung *nach einem empfindungslosen Intervall* eine *zweite*, gleichfalls stechende Empfindung, welche sich in ihrem Character dadurch von der ersten unterscheidet, dass ihr nichts von Tastempfindung beigemischt ist, sie vielmehr gleichsam wie von innen zu kommen scheint. Bei mässiger, noch nicht schmerzhafter Intensität der primären Empfindung kann die secundäre schmerzhaft sein . . . . Das Phänomen der secundären Empfindung tritt schon bei sehr schwachen, vom Schwellenwerth nicht weit entfernten Reizen auf."

GAD and GOLDSCHIEDER have made methodical experiments concerning the phenomenon, causing them to consider it as a sensation brought about by summation of stimuli.

They also have pointed out already the analogy with the after-images, of the retina, produced by optic stimuli of short duration.

An exact analysis however of the subjective phenomena, following the experiment indicated by GOLDSCHIEDER shows, that the analogy between what happens for the skin and for the eye, is a far greater one than we might think at first sight.

For by this analysis it becomes evident that something may be added still to GOLDSCHIEDER's description. The subjective impression does not stop at the secondary sensation, but constantly a tertiary sensation may be observed.

As soon as I am trying the experiment of GOLDSCHIEDER upon myself, applying on the skin with the point of a blunt pin a prick of very short duration, but very feeble, the skin being depressed hardly more than  $\frac{1}{2}$  millimeter, the first, primary sensation arises almost simultaneously with the contact. After an interval of from 0.8 — 0.96 second the secondary sensation commences in accordance with the description of GOLDSCHIEDER.

*About from one to three seconds after this, a tertiary sensation follows, consisting in a peculiar feeling of irritation and itching, compelling us involuntarily to rub the irritated portion of the skin with the hand. This last sensation rises very slowly, reaching its maximum in little more than one second, and disappearing again with far greater slowness. The duration of the first sensation amounts to a very small part of 1 second, the second sensation is likewise a short one, though generally somewhat longer than the first; the duration of the tertiary sensation is still longer, amounting to from 2—10 seconds, and even more if the intensity of the prick was somewhat stronger. The curve of the three sensations may be represented graphically by a figure.*

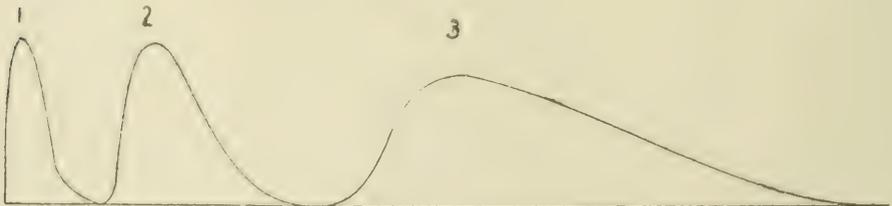


Figure 1.

The analogy with the visual after-images, such as these have been described recently by KRIES, HESS, HAMAKER and others, is most

striking. There too we find a primary image followed by the "satellite," and this followed in its turn by the tertiary positive image. The latter is ever followed by a negative after-image. In the opinion of Hess, the primary image and the satellite are also followed by negative after-images. A scheme of the total of the sensation is given by him as a sinusoid with a rapidly decreasing amplitude and an increasing period; see fig. 2, in which the direct image

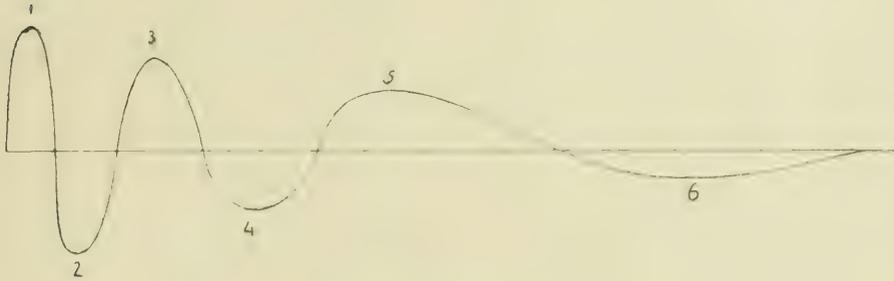


Fig. 2.

is represented by 1, the satellite by 3, the positive after-image by 5, and by 6 the final, easily visible after-image. Hess pretends to perceive likewise the negative after-images 2 and 4, which I have never been able to see; for several reasons, not to be given here, I seriously doubt whether these after-images 2 and 4 really exist.

Leaving this question, I only wish to point out the close resemblance, offered by the tactual sensation, following a single feeble touch of a pin-point, with the series of positive after-images of the eye, represented by the combination 1, 3 and 5. The course of the phenomena is the same in both cases: the *relative* duration of each subdivision is perfectly equal for both senses, only the absolute duration is somewhat longer for the skin.

Still another analogy is shown by the quality of the three separate images being different, as well for the eye as for the skin. I wish to lay great stress on the statement of this last fact, because it opens the possibility of a new conception, equally different from that of GOLDSCHIEDER as from that of HESS. Even the experiments of GOLDSCHIEDER, alleged by him in favour of his hypothesis of summatio are subject to another explanation.

GOLDSCHIEDER observed that one single induction-shock, however strong it may be, applied as a cutaneous stimulus, is never able to rouse the secondary sensation, whilst this was effected easily and constantly by 3 or 4 shocks of the induced current, even rather feeble ones, following each other in rapid succession.

Now let us consider only what happens for the vasomotor nerves. If these are excited by frequent shocks of the induced current, they react by a vasoconstriction followed by vasodilatation. If the shocks of the current are following one another very slowly, only dilatation is obtained. And finally, if a peripheral motor nerve innervating both striped muscle-fibres and vascular muscles, is stimulated, it may occur sometimes, that after one single shock of the current only contraction of the voluntary fibres follows. If several elementary stimuli, following one another in an appropriate rhythm, are applied, first a contraction of the striped muscles, may be observed, next of the vasoconstrictor, and finally of the vasodilatator fibres.

As soon as we suppose in the retina or in the skin the presence of more than one species of end-organs the possibility may be assumed that only one of these species reacts on stimuli of short duration, whilst other organs react on stimuli of longer duration. If stimuli of definite duration and intensity are made use of, both organs will react, each after its own latent period, in the same way as happens for muscles, vasoconstrictors and vasodilatators, so that we will obtain two sensations subsequent to each other. In cases, where three excitable organs coexist, even three separate sensations may be felt, as in the case of stimulation of the skin and of the retina.

**Chemistry.** — “*The course of the solubility curve in the region of critical temperatures of binary mixtures.*” (Second communication). By Dr. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of December 19, 1903).

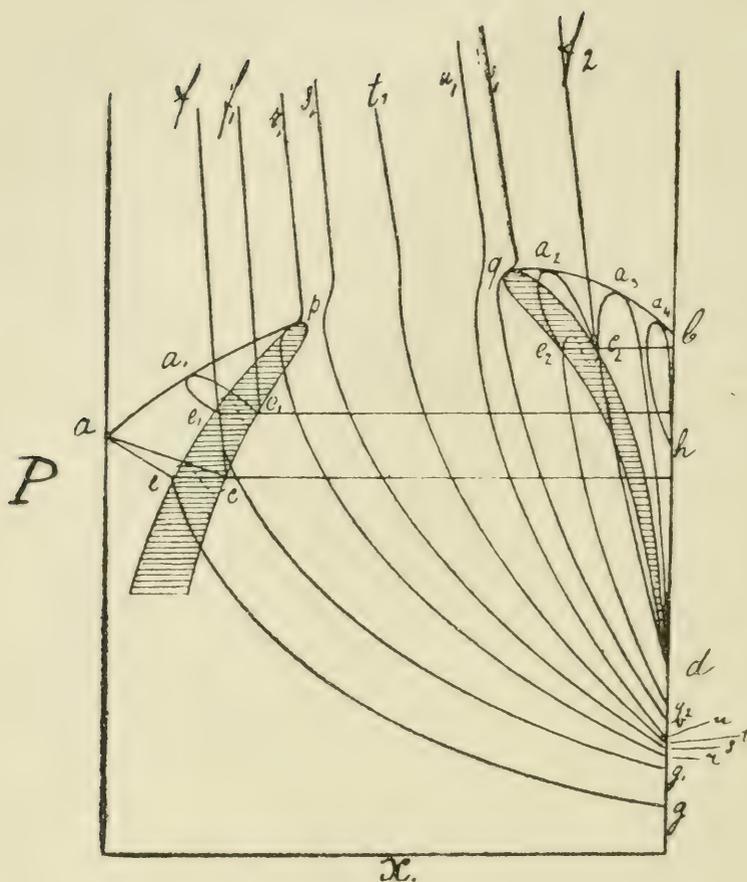
In my preceding communication<sup>1)</sup> on this subject I have represented in the figures 3 and 4 the  $p$ - $x$ -sections for different temperatures, starting with the critical temperature of  $A$  and finishing at the melting point of  $B$ . Fig. 3 holds for the case that the three-phase-curve lies entirely below the plaitpoint-curve, and Fig. 4 applied to the case that the three-phase-curve cuts the plaitpoint-curve. In order to obtain the  $T$ - $x$ -projection from the combination of the different  $p$ - $x$ -sections, the variations of pressure were left out of account.

To complete what precedes the actual succession of the  $p$ - $x$ -sections for different temperatures will be represented here.

<sup>1)</sup> These Proc. Oct. 27th 1903, p. 171.



Fig. 2.



At  $p$  the curve of the saturated solutions  $cc_1$  passes here without a break into the curve of the saturated vapours  $ee_1$ .

The curve  $aa_1$  touches the curve  $ee_1$   $pc_1c$  in a point on the left side of  $p$  and becomes there metastable, becoming stable again at a point on the right side of  $q$ . At  $q$  we observe the same thing as at  $p$ , viz. a breakless meeting of the curves  $dc_2$  and  $de_2$ . The curves  $ppr_1$  and  $qqv_1$ , which represent the "fluid" phases, coexisting with solid  $B$ , have the course given here, as has been shown by VAN DER WAALS<sup>1)</sup>. The possibility of drawing two vertical tangents to these curves, implies the phenomenon of *retrograde solidification*. In the immediate neighbourhood of  $p$  and  $q$  we do not see any change in this, but at greater distances, e.g. halfway between  $p$  and  $q$  it is possible that the two tangents coincide, which causes the retrograde solidification

<sup>1)</sup> These Proc. VI 230 Oct. 31<sup>st</sup> 1903 and VI 357 Nov. 23<sup>rd</sup> 1903.

to vanish<sup>1)</sup>; the inflection point, however, continues to exist<sup>2)</sup>. In my first paper I was led by the experiments of VILLARD to accept the possibility of a retrogression of the  $p$ - $v$ -curve, which for a system of the type ether-anthraquinone represents the "fluid" phases coexisting with solid  $B$  and now we see that this is necessarily so for the immediate neighbourhood of  $p$  and  $q$ . So it has been ascertained theoretically, that we can make solid  $B$  evaporate somewhat in the immediate neighbourhood of  $p$  and  $q$ . If for a system of the type ether-anthraquinone an *entire* volatilisation of *arbitrary quantities* of  $B$  were observed, this would point to a  $p$ - $v$ -loop as is found for the system oxygen-bromine at  $17^\circ$ , or in other words to *continuity* between the *solid* and the "fluid" phases.

As I said before it is necessary to examine the  $v$ - $v$ -sections for different temperatures in order to gain a better understanding of the question.

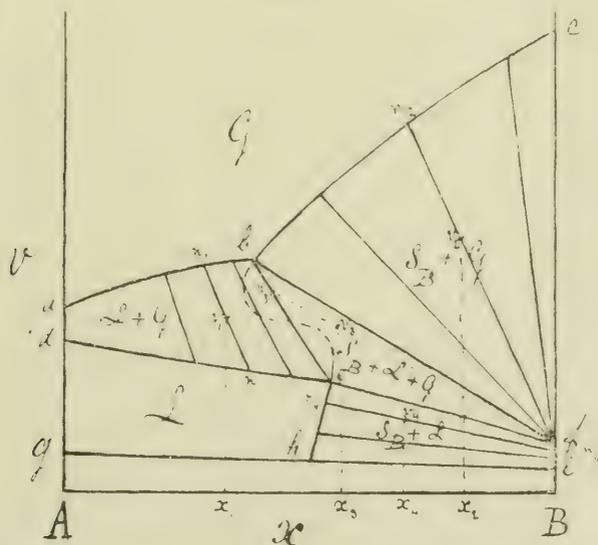
Let us first consider the usual case, that the three-phase-curve lies entirely below the plaitpoint-curve.

For a temperature below the critical temperature of  $A$ , we get the following  $v$ - $v$ -section. (Fig. 3).

$Aa$  represents the mol. vol. of the saturated vapour of  $A$ ,  $Ad$  that of liquid  $A$ .  $Bc$  is the mol. vol. of the saturated vapour of  $B$  and  $Bf$  the mol. vol. of solid  $B$ .

$ab$  denotes the mol. vols. of the vapour mixtures  $A+B$ , coexisting

Fig. 3.



<sup>1)</sup> loc. cit.

<sup>2)</sup> This is the case when the curve has originally only one inflection point. If it has two inflection points, which is most likely also possible, they can both disappear.

with the liquid mixtures, for which the line  $de$  represents the molecular volumes.

The point  $b$  indicates the mol. vol. of the vapour saturated with  $B$  and  $e$  the mol. vol. of the liquid saturated with  $B$ .  $abcd$  is the region of the phase-complexes  $L + G$ , the nodal lines drawn in it connect coexisting phases.

The mol. vols. of the vapours coexisting with solid  $B$  lie on the curve  $bc$ , and the triangle  $bef$  is the region for the phase-complexes  $S_B + G$ .

The coexisting phases lie in this case on lines traced from  $f$  to the curve  $bc$ . The triangle  $bfe$  is the three-phase-triangle and therefore the region for  $S_B + L + G$ .

The line  $eh$ , which divides the space under  $def$  into two parts, represents the mol. vols. of the liquids coexisting with solid  $B$ . For smaller volumes this line runs to the left, because in normal cases the solubility of  $B$  in  $A$  diminishes with decrease of volume.

The quadrangle  $efhi$  is the region of the phase-complexes  $S_B + L$ , the coexisting phases are indicated by the small lines drawn in the figure. Inside  $dehg$  we have only *one* phase, viz. liquid, and above  $abc$  only gas.

The lines  $cb$  and  $eh$  are two portions of a continuous curve with an intermediate portion, which will have two vertical tangents in normal cases. It is easy to prove this with the aid of the theory of VAN DER WAALS, and this can be done in a way analogous to that, in which VAN DER WAALS<sup>1)</sup> has proved the existence of two vertical tangents to the  $p,v$ -curve for solid-liquid.

We start then from the differential equation of  $v$  when  $x$  and  $T$  vary. (Cont., II pag. 104).

Let us denote the concentration and the mol. vol. of the solid phase by  $x_s$  and  $v_s$  and that of the coexisting gas phase and liquid phase by  $x_f$  and  $v_f$ , the equation is then :

$$(v_s - v_f) \left[ \frac{\partial^2 \Psi}{\partial x_f^2} \frac{dv_f}{dx_f} + \frac{\partial^2 \Psi}{\partial x_f \partial x_s} \frac{dx_f}{dx_s} \right] - (x_s - x_f) \left[ \frac{\partial^2 \Psi}{\partial v_f \partial x_f} \frac{dv_f}{dx_f} + \frac{\partial^2 \Psi}{\partial x_f^2} \frac{dx_f}{dx_f} \right] \cdot \frac{(\varepsilon_{2,1})_v}{T} dT = 0.$$

If  $T$  is kept constant, the last term of the first member becomes zero and we get after an unimportant transposition :

$$\left[ (v_s - v_f) \frac{\partial^2 \Psi}{\partial x_f^2} + (x_s - x_f) \frac{\partial^2 \Psi}{\partial v_f \partial x_f} \right] dx_f - \left[ (v_s - v_f) \frac{\partial^2 \Psi}{\partial v_f \partial x_f} + (x_s - x_f) \frac{\partial^2 \Psi}{\partial x_f^2} \right] dx_f$$

or

$$\frac{\partial^2 \Psi}{\partial x_f^2} \left[ (v_s - v_f) \cdot (x_s - x_f) \left( \frac{\partial v_f}{\partial x_f} \right)_{pT} \right] dv_f = - \left[ (v_s - v_f) \frac{\partial^2 \Psi}{\partial v \partial x_f} + (x_s - x_f) \frac{\partial^2 \Psi}{\partial x_f^2} \right] dx_f.$$

<sup>1)</sup> loc. cit.

We have :

$$(v_s - v_f) - (x_s - x_f) \left( \frac{\partial v_f}{\partial x_f} \right)_{p,T} = v_{sf}.$$

$v_{sf}$  denotes the decrease of volume per molecular quantity, when an infinitely small quantity of the solid phase passes into the co-existing phase at constant pressure and constant temperature.

By substitution we get :

$$\frac{\partial^2 \Psi}{\partial v_f^2} \cdot v_{sf} \cdot dv_f = - \left[ (v_s - v_f) \frac{\partial^2 \Psi}{\partial v_f \partial x_f} + (x_s - x_f) \frac{\partial^2 \Psi}{\partial x_f^2} \right] dv_f$$

or

$$\frac{dv_f}{dx_f} = - \frac{\left[ (v_s - v_f) \frac{\partial^2 \Psi}{\partial v_f \partial x_f} + (x_s - x_f) \frac{\partial^2 \Psi}{\partial x_f^2} \right]}{\frac{\partial^2 \Psi}{\partial v_f^2} \cdot v_{sf}}.$$

VAN DER WAALS has lately demonstrated that  $v_{sf}$  can twice become zero when  $v_s$  is smaller than  $v_f$ , in consequence of which  $\frac{dv_f}{dx_f}$  becomes twice infinitely large.

Further  $\frac{\partial^2 \Psi}{\partial v_f^2}$  can also twice become zero, but this does not give rise to an infinitely large value for  $\frac{dv_f}{dx_f}$ , as,  $\frac{\partial^2 \Psi}{\partial v_f^2}$  being zero, and we being therefore in  $D$  or  $D'$  (Fig. 2 VAN DER WAALS),  $v_{sf} = \infty$  and  $\frac{dv_f}{dx_f}$  has therefore a finite value.

If  $v_s$  is larger than  $v_f$ , which may also occur, then only one vertical tangent is possible. This is attended by a change also in the course of the lower part of the line  $cbch$ . In the above figure  $ch$  runs to the left for smaller volumes, but then this curve must directly run to the right, which means that the solubility of  $B$  in  $A$  increases for smaller volumes (larger pressures), a behaviour which may also be expected theoretically for smaller volumes when initially  $v_f > v_s$ , whereas the reverse, so the usual course is found for larger volumes. If, however,  $v_s > v_f$  the course must be the abnormal one from the beginning.

For the better understanding of fig. 3 I shall add a few words about each of the different regions.

Let us assume that we have a mixture of the concentration  $x_1$  for a volume  $x_1 v_1$ ; we are then in the region of  $L + G$ . If we draw the nodal line  $n v_1 n_1$  through  $v_1$ ,  $n$  denotes the mol. vols. and

the concentration of the liquid and  $n_1$  those for the vapour coexisting with this liquid. In addition the relation between the volumes of liquid and vapour may be read from the pieces, into which the point  $v_1$  divides the nodal line; it is viz.  $\frac{\text{liquid}}{\text{vapour}} = \frac{n_1 v_1}{n v_1}$ .

With a concentration  $x_2$  and volume  $x_2 v_2$  we are in the region  $S_B + G$ ; the mol. vols. and the concentration of the vapour coexisting with solid  $B$ , are denoted by  $v_2$ ; the relation of the volumes by  $\frac{\text{solid}}{\text{vapour}} = \frac{n_2 v_2}{f v_2}$ .

If we now take a concentration  $x_3$  with a volume  $x_3 v_3$ , we are in the three-phase-triangle. The mol. vols. of the three phases are indicated by the three angles; the relative volumes are found by drawing a line from  $f'$  through  $v_3$ , till it intersects the line  $be$ . The relation  $\frac{\text{solid}}{\text{liquid} + \text{vapour}} = \frac{n_3 v_3}{f' v_3}$  and the relation  $\frac{\text{liquid}}{\text{vapour}} = \frac{bn_3}{en_3}$ . If finally

we have a concentration  $x_4$  with a volume  $x_4 v_4$ , we are in the region  $L + S_B$ ; the mol. vols. of the coexisting phases are now expressed by  $n_4$  and  $n'_4$ , the relative quantities being indicated by  $\frac{\text{liquid}}{\text{solid } B} = \frac{v_4 n'_4}{v_4 n_4}$ .

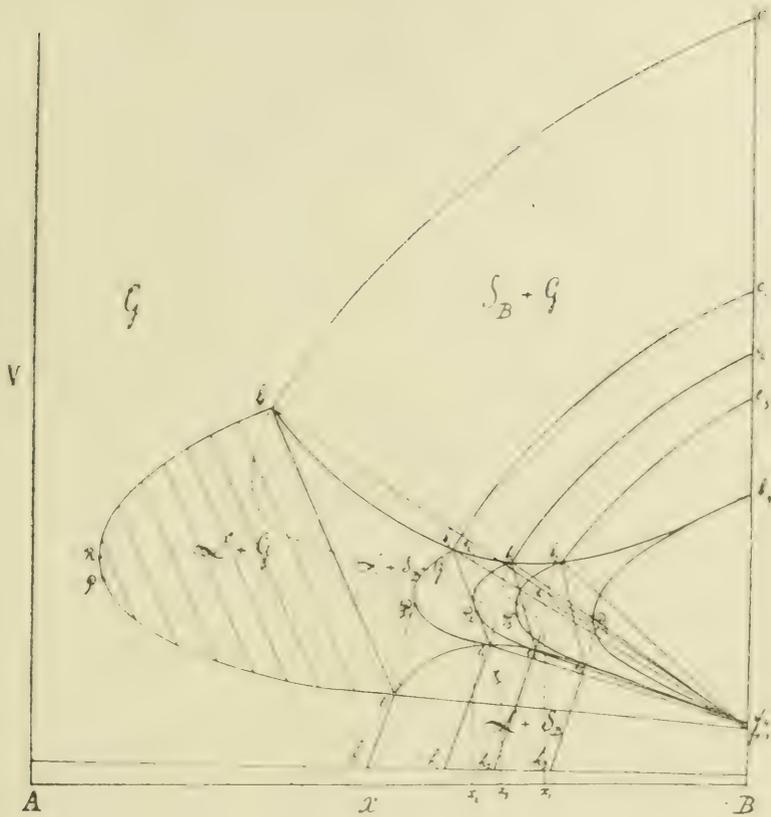
When the temperature rises, this  $v$ -section suffers a change; in the first place the curves  $ab$  and  $bc$  are moved lower and the curves  $de$  and  $ef$  are moved upward. The displacement of the point  $f$  however is very small compared with the other displacements. The points  $b$  and  $e$  are also moved to the right, because the solubility of  $B$  in  $A$  is supposed to increase with rise of temperature.

These are the changes for the case that we are still below the critical temperature of  $A$ ; when we have reached this temperature, the curves  $ba$  and  $ed$  pass without a break into each other and with rise of temperature up to the melting point of  $B$  we get a series of conditions represented in Fig. 4. (p. 491).

The binodal curves  $bPv$  with the plaitpoints in  $P$  lie all inside each other; they cannot be prolonged to the  $B$  side below the melting temperature of  $B$ , because the substances  $A$  and  $B$  become miscible in all proportions only at the melting point of  $B$ . Just above the critical temperature of  $A$  the nodal lines for the saturated vapours and liquids have a strongly slanting position; at higher temperatures, however, they slant less, because the difference in concentration between  $b$  and  $v$  becomes smaller.

The curve  $b b_1 b_2 b_3$  is the  $v$ - $t$ -curve for the saturated vapours, the

Fig. 4.



curve  $ee_1e_2e_3$  is the  $v$ - $t$ -curve for the saturated liquids. The former curve has a minimum, the second a maximum<sup>1)</sup>.

That the  $v$ - $t$ -curve of the saturated vapour must have a minimum can be easily proved for the system  $\text{AgNO}_3\text{—H}_2\text{O}$ <sup>2)</sup>. In this case the matter is so simple, first because the vapour consists only of water and secondly because the maximum of the pressure is still below  $1\frac{1}{2}$  atmosphere and therefore the law of BOYLE-GAY-LUSSAC may be applied for an approximation.

The vapour tensions of the saturated  $\text{AgNO}_3$ -solutions are not yet accurately known, but this is of no importance here. We may assume here for the moment, that the values are perfectly accurate and then see what the position of the  $v$ - $t$ -curve for the vapour must be.

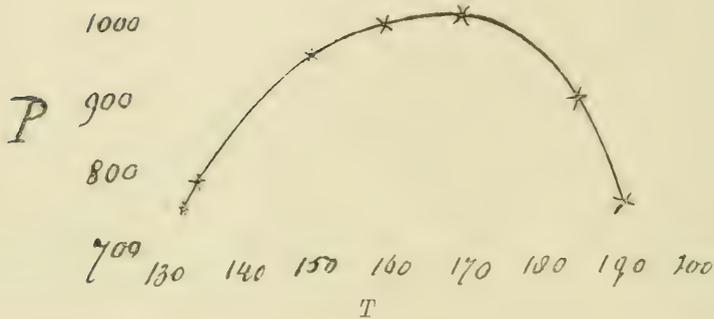
We get the following result :

<sup>1)</sup> Probably this need not always be the case.

<sup>2)</sup> These Proc. IV, 371. Dec. 28, 1901.

Temp.	Vapour tension in m.m. Hg.	Mol. vols. of the vapour in liters
133	760	33.35
135	800	31.82
150	960	27.49
160	1000	27.02
170	1010	27.37
185	900	31.75
191	760	38.09

Fig. 5.



maximum at 170°

The figures 5 and 6 are graphical representations of the  $pt$ - and the  $vt$ -curves.

We see, that the maximum in the  $pt$ -curve lies at about 170°, and that the minimum in the  $vt$ -curve lies at 161°. The maximum in fig. 5 is therefore not found at the same temperature as the minimum in fig. 6. (p. 493).

That this must be the case can be easily proved by applying the equation  $PV = RT$ . If we differentiate this equation, we get :

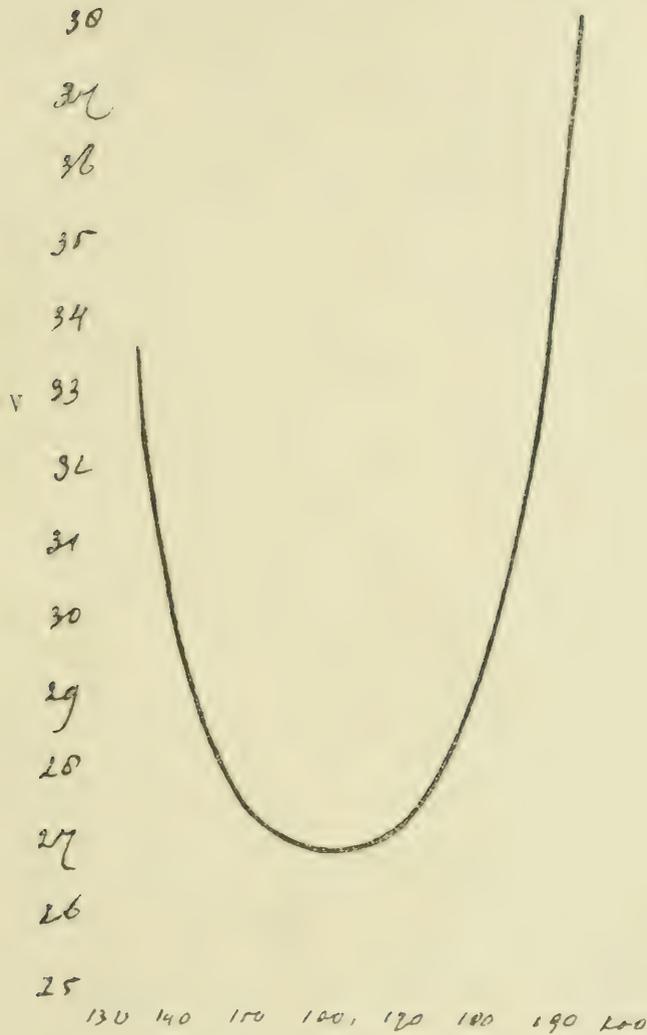
$$v \frac{dv}{dT} - \frac{dT}{T} - \frac{dp}{p}$$

or

$$\frac{dv}{dT} = \frac{v}{T} \left( 1 - \frac{T}{p} \frac{dp}{dT} \right)$$

For the minimum in the  $vt$ -curve  $\frac{dv}{dT} = 0$  is therefore :

Fig. 6.



T  
minimum at 161°.

$$1 - \frac{T}{p} \frac{dp}{dT} = 0$$

or

$$\frac{dp}{dT} = \frac{p}{T}$$

So when  $\frac{dv}{dT} = 0$ ,  $\frac{dp}{dT}$  has a positive value. In the maximum of the vapour tension curve we have :

$$\frac{dp}{dT} = 0 \quad \text{hence} \quad \frac{dv}{dT} = \frac{v}{T}.$$

So for the temperature, at which the vapour tension curve has reached its maximum, the  $v$ - $t$ -curve is ascending.

Finally I shall briefly point out that the value for  $\frac{dp}{dT}$  at  $161^\circ$ , calculated from the vapour tension curve harmonizes well with the theoretical value  $\frac{p}{T}$ . For the range of temperature between  $150^\circ$ — $170^\circ$ ,  $p$  may be found from the following interpolation formula

$$p = p_{150} + 5,5(t-150) - 0,15(t-150)^2$$

For  $161^\circ$  follows from this

$$\frac{dp}{dT} = 2,2$$

and

$$\frac{p}{T} = \frac{1001}{434} = 2,3.$$

It follows from the construction that the  $v$ - $t$ -curve for the saturated solutions can have a maximum, but it is not easy to deduce this theoretically.

We shall now continue the discussion of fig. 4.

If we take a concentration  $x_1$  with a volume  $x_1v_1$  and at the temperature for which the first  $v$ - $v$ -section holds, we are in the three-phase-triangle  $hfe$ , and so we have side by side  $S_B + L + G$ . At the temperature for which the second  $v$ - $v$ -section is drawn, the point  $v_1$  is no longer in the three-phase-triangle, but in the region for  $S_B + G$ ; the liquid has therefore disappeared, and only solid  $B +$  vapour is left.

At the temperature corresponding to the third  $v$ - $v$ -section the point  $v_1$  has returned to the three-phase-triangle and solid  $B +$  vapour has therefore been partly converted into a liquid. At the temperature corresponding to the fourth  $v$ - $v$ -section the point  $v_1$  is found in the region of the unsaturated liquids with their vapours and at the melting point of the substance  $B$ ,  $v_1$  lies in the region of the vapour and so everything has evaporated.

If on the other hand we had started from the concentration  $x_2$  with a volume  $x_2v_2$ , we should have left the three-phase-triangle with increase of temperature and we should have reached the region for  $S_B + G$ , and have passed from there straight into the gas-region. As  $v_2$  is situated above the  $v$ - $t$ -curve  $bb_1$ , there is here nothing retrograde as in the case discussed above. It is obvious that the retrograde phenomenon will occur for conditions lying above the tangent drawn to the  $v$ - $t$ -curve  $bb_1$  from a certain point  $f'$  (between

$f'_0$  and  $f'_1$ ), and below that part of the curve  $bb_1$  that lies between the point of contact and the point  $b_1$ .

If we further consider the case that the composition is  $x_2$  and the volume  $v_2$ , we have the case that with rise of temperature we get from the three-phase-triangle into the region for  $L + S_B$  and so that the vapour disappears. With further increase of temperature we pass directly from the region  $L + S_B$  into the gas-region, just as for the condition  $x_2 v_2$  we passed from the region  $S_B + G$  into the gas-region. In the remaining cases nothing noteworthy takes place; we must only point out, that for systems of the type of fig. 4 the critical phenomenon can only be observed for *unsaturated* solutions.

Fig. 7 applies to systems of the type of ether-anthraquinone. The difference between this figure and the preceding one lies in the fact

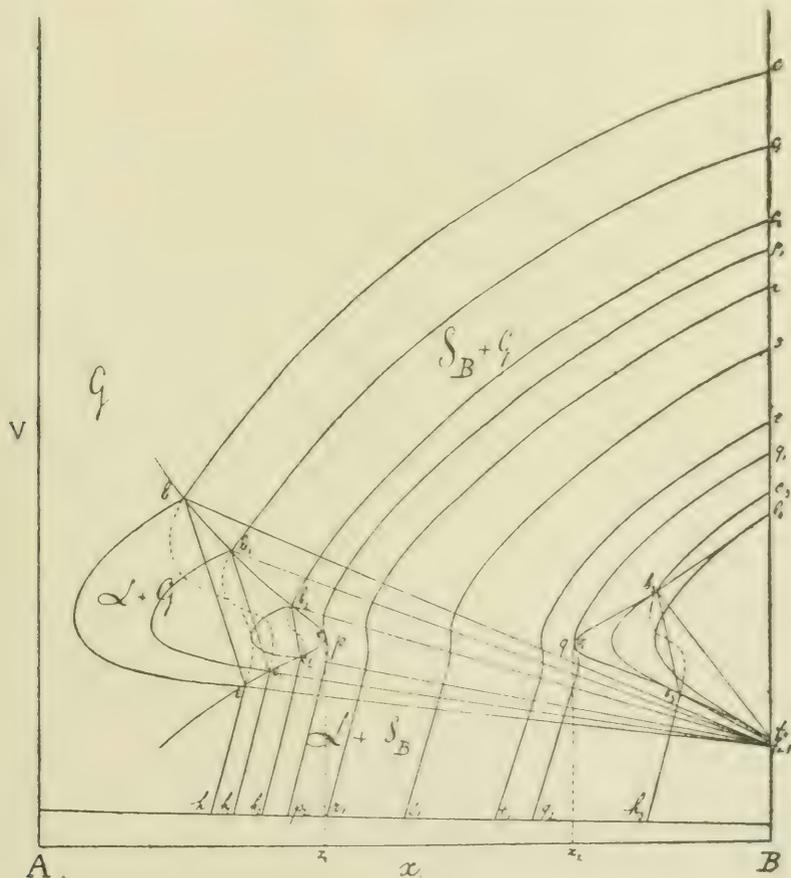


Fig. 7.

1) CENTNERSZWER (Zeitschr. f. Elektrochem. N<sup>o</sup>. 40 S. 799 (1903) has lately drawn attention to this retrograde phenomenon.

that if we come from low temperatures the  $v$ - $t$ -curve for the saturated vapour and that for the saturated liquid approach each other more and more, and finally pass without a break into each other. At  $q$  we get a repetition of what precedes in reversed order. On the left of  $p$  and on the right of  $q$  we have the same thing as in fig. 4; at  $p$  and  $q$  however, we see something special, viz. that here the critical phenomenon can be observed for a just *saturated* solution.

We have further seen in fig. 4 that the succession of conditions  $L + S_B + G \rightarrow S_B + G \rightarrow G$  could occur there for conditions lying above the curve  $bb_4$ . In fig. 7 this takes place, besides above the curves  $bp$  and  $qb_4$ , also between the concentrations  $x_1$  and  $x_2$ , corresponding with the points  $p$  and  $q$ , for any *arbitrarily* chosen volume, because the region for  $S_B + G$  between  $p$  and  $q$  passes continuously into the region for  $S_B + L$ . Hence this phenomenon will occur much more frequently for the type of fig. 7 than for the type of fig. 4.

The usual succession  $L + S_B + G \rightarrow L + G \rightarrow G$  is here only possible for conditions lying within the  $v$ - $t$ -curve  $ee_1e_2pb_2b_1b$ .

The retrograde phenomenon discussed above will here be observed for all conditions lying below the branch  $b_4b_3q$  of the second  $v$ - $t$ -curve and above the tangent drawn to the branch  $qe_3f_4$  from a point  $f'$  (between  $f'_0$  and  $f'_4$ ). A very essential point of difference with the case of fig. 4 is further to be found, first in the circumstance that with a concentration  $x_1$  and a volume  $x_1v_1$  we pass here suddenly from the region  $L + S_B + G$  into the gas region and secondly that for a composition *slightly* richer in  $B$  than  $x_2$  and with a volume  $x_2v_2$  just at the moment at which all the solid  $B$  would evaporate, a *saturated* solution is formed, which reaches its critical temperature immediately after its formation.

From fig. 7 follows that if we started from a concentration  $x_2$  with a volume  $x_2v_2$ , with which therefore the point  $q$  can be reached, the transition  $L + S_B + G \rightarrow S_B + G$  takes place at a temperature lower than that corresponding to the point  $p$ , so that the points  $p$  and  $q$  can never be determined by one experiment, which it is practically superfluous to mention.

The curves  $p_1p$ ,  $p_2p$ ,  $r$ ,  $r_1$ ,  $t$ ,  $t_1$  and  $q_1q$ ,  $q_2q$ , which denote the mol. vols. and the concentrations of the "fluide" phases coexisting with solid  $B$ , have still two vertical tangents, as they are in the immediate neighbourhood of  $p$  and  $q$ , from which the retrograde solidification follows. For the curve  $S$ , drawn halfway between  $p$  and  $q$ , the two vertical tangents coincide in accordance with the  $p$ - $x$ -curve in Fig. 2, which means, that there retrograde solidification is no longer possible.

We shall conclude with some remarks on the determination of the plaitpoint- or critical temperature.

As is known, the critical phenomenon for binary mixtures can only be observed, when before the region  $L+G$  is left, there is exactly the same quantity of liquid as of vapour, or in other words, when the volume is exactly the same as the plaitpoint volume (see fig. 4). In this case we enter the gas region at the plaitpoint  $P$ . In general every concentration requires then another volume. If the volume is greater or smaller than the plaitpoint volume, we do not observe a critical phenomenon. In the first case we come to the gas branch of the binodal curve, and consequently total evaporation of the liquid takes place when the temperature rises slowly; the liquid mass decreases more and more and disappears in the lower part of the tube. In the second case we reach the liquid branch of the binodal curve and the whole tube is finally filled with liquid.

A sudden transition from the region  $L+G$  into the gas region, in consequence of the fact that the liquid and the gas phase become *identical* is only observed for a volume equal to the plaitpoint volume, also when the temperature rises very slowly. Yet for other volumes phenomena may be observed, closely resembling the critical ones, but this is only to be attributed to the fact that the temperature rises too quickly for the equilibrium to be established.

For a simple substance the plaitpoint temperature is the highest, but this is not the case for binary mixtures. The highest temperature for a binary system will be observed for the volume of the critical tangent  $R$ , so for a volume larger than the plaitpoint volume (see fig. 4). For still larger volumes the liquid will again disappear at lower temperatures, so that from the plaitpoint volume to larger volumes the temperature, at which all the liquid has disappeared, and which we might also call condensation temperature, passes through a maximum value. If the volume is smaller than the plaitpoint volume, the tube is completely filled with liquid, but the temperature at which this takes place, is always lower than the plaitpoint temperature.

*Amsterdam*, Dec. 1903.

Chemical Laboratory of the University.

**Botany.** — “*Exosporina Laricis* OUD. — *A new microscopic fungus occurring on the Larch and very injurious to this tree.*”  
By Prof. C. A. J. A. OUDEMANS.

On June 11, 1903, Mr. C. A. G. BEINS collected on the estate “de Groote Bunte” at Nunspeet and sent to me a number of needles and twigs of the common Larch (*Larix decidua* = *Larix europaea*), the former of which, although they belonged to recently grown dwarfshoots, had for the greater part a sickly appearance, and had exchanged their light-green colour for a light-brown one.

The question naturally arose: what could be the cause of this phenomenon, and whether a fungus might be at the root of it.

An investigation concerning this matter soon showed me that the twigs were normal, and consequently had not been visited by the to the Larch very injurious *Peziza* (*Dasyyscypha*) *Willkommii*, but that the needles were spotted on both sides, but especially on the lower side, with very small black specks (Fig. 1).

These specks, spread at random, sometimes more, sometimes less numerous, mostly circular, had a diameter of 100—150  $\mu$  at the utmost, and most resembled *Leptostroma*- or *Leptothyrium*-specks, although a closer examination showed that they shared no property of any importance with these genera. They colored firmly with the epiderm, and it soon appeared that they had not been hidden under it and gradually found an exit, but that they had existed from the beginning on the surface of the needles.

This result was not obtained by examining cross-sections, which the very minute specks did not allow to make, but by heating the needles for a few minutes in a ten percent solution of caustic potash, washing them, making them transparent with chloral-hydrate, and gently pressing them with a cover-slip. Under the microscope light-brown, wavy, occasionally bifurcated threads or ribbons of varying breadth were seen on the leaf, which in various places produced little disks, from which new threads were sent out in some other direction (Fig. 2).

The threads consisted of articulate hyphae and the disks of a small-celled parenchym. By pressing the latter more strongly and so dividing them into smaller fragments, it appeared that they were not flat but globular, and that they protruded like little cupolas above the epiderm to which they were firmly attached.

These fragments also gave an opportunity of gaining an idea about the internal structure of the disks. From their small-celled tissue, namely, certain favoured hyphae had grown up in a close bunch, in

such a way that their height increased regularly from the edge to the middle. These hyphae, by forming numerous partitions, had got an articulate appearance. On closer inspection the multicellular rods appeared, in a more mature state, to consist in the lower parts of cubical, in the higher ones of more rounded cells, and finally to become disintegrated, so that, on account of similar cases, there could be no doubt that the cast-off cells were the means of multiplication and had consequently to be considered as conidia.

These conidia, from which new infections may be expected, are mostly  $5-6 \mu$  high and  $5 \mu$  broad, have a light-brown colour and are perfectly smooth. By far the greater part of them are undivided; only a few show perpendicular or inclined partitions.

If we now ask what harm is done to *Larix decubus* by the above described fungus, the answer can only be that the stomata are blocked up and rendered useless by it; that the function of the leaves is interfered with, and that the chlorophyll is changed in such a manner, that its assimilative power is reduced, and that evaporation is in no small measure prevented. This is proved by the brownish colour of the leaves replacing the green one. In one and the same spiral of needles, such as are found with *Larix*, the morbid process proceeds from the outside to the interior, so that for a considerable period needles of two colours are observed on the rosettes.

As the needles fall off pretty soon, and lodge no mycelium threads which might have gone on to the twigs, it follows that, in order to prevent future damage to the trees, the fallen needles should be removed and burnt. Spraying might perhaps save attacked trees from further decay. For trees that are visited by the fungus, begin to languish, their growth is impeded, their resistance diminishes, and so they soon fall a victim to all sorts of Dematiaceae which give them a dirty blackish appearance.

The next question is: what place in the system the fungus ought to occupy, and what name has to be assigned to it.

To begin with, it undoubtedly belongs to the "Fungi imperfecti", lately entitled "Deuteromycetae" by SACCARDO (Syll. XIV, p. 4). Secondly we must exclude the *Sphaeropsidaceae*, which possess a perithecium, as well as the *Melanconiaceae*, the conidia of which, without being ocluded in a perithecium, develop within parts of plants and rest on a stroma. Our fungus rather belongs to the third and last, at the same time the largest class of the Deuteromycetae, which have no perithecium and the conidia of which, produced on threads or hyphae, live either independent of each other, which is the general case, or are gathered in bundles, forming a so called "Coremium".

For the sake of brevity we shall state at once that our fungus belongs to the Tuberculariaceae, with coloured hyphae and conidia linked like a rosary, and that first CORDA (Icones Fung. I, p. 9 and fig. 148), and later SACCARDO (Syll. IV, 757) assigned the generic name *Trimmatostroma* to a similar fungus.

The species, described and represented by the former, he called *Trimmatostroma Salicis*, after its host. Now it deserves notice that SACCARDO found a fungus on rose hips and first called it *Exosporium fructicola* (Fungi Italici, pl. 40), which he later transplaced to *Trimmatostroma* and called *Tr. fructicola*: firstly because in the genus *Exosporium*, introduced by LINK and exemplified by *E. Tiliae* (plate 1, fig. 8 of his *Observationes mycologicae*), the conidia are not linked together, but adjacent, and secondly because in his opinion the structure of *Exosporium fructicola* did not agree with that of *Exosporium Tiliae*, but with that of *Trimmatostroma Salicis*.

Now our plate shows *Trimmatostroma Salicis* Corda (fig. E) as well as *Trimmatostroma fructicola* (fig. F), reproduced from the original drawings, in order to elucidate our conviction that between these two, points of difference are to be found rather than points of resemblance, and this to such an extent, that it seemed to us that *Trimmatostroma* had to be shifted again, this time to the genus *Exosporina*, introduced by us for *E. Laricis*, with which SACCARDO's fungus has the greatest resemblance.

The characteristics of the three repeatedly mentioned genera can now be summarised as follows:

*Exosporina*. — Conidia in strings, undivided, falling off singly. Stroma not or only slightly developed.

*Exosporium*. — Conidia consisting of two or more cells, not united to strings, forming a close assemblage on a stroma.

*Trimmatostroma*. — Multicellular conidia, loosely cohering, forming a dense aggregate on a well developed stroma.

Of the genus *Trimmatostroma*, in CORDA's sense, only two species are known besides *Tr. salicis*, viz. *Tr. americana* Thüm. Mycol. Univ. N°. 793 (Sacc. Syll. IV, 757) on twigs of *Salix discolor*, and *Tr. amentorum* Bresad. et Sacc., on female catkins of *Alnus incana*. A species described by DOHERTY under the name of *Tr. abietina* (um?) (Botanical Gazette 1900, p. 401, and Sacc. Syll. XVI, 1107) agrees more with a *Sporodesmium* according to the description, and is considered as such by SACCARDO. All these three fungi need not be considered here. We would only remark that *Trimmatostroma abietina*, which like our *Exosporina Laricis* occurs on the leaves of Conifera,

causes great damage to plantations of *Abies balsamea* in the environs of Guelph in Ontario. Though it may be very probable that the fungus mentioned does not belong to the genus *Trimmatostroma*, yet it appears from DOHERTY'S article that it greatly impedes the growth of the trees by choosing their needles as substrate. About the checking of the evil nothing is mentioned by DOHERTY, so that we cannot profit by advice from Ontario. No suffering trees were found at Nunspeet except at "de Groote Bunte".

EXOSPORINA OUD. n. g.

Fungi expositi vel endogeni, stromate nullo vel parum evoluto, conidiis in catenas stipatas digestis, singulatim secedentibus, homomorphis, continuis, coloratis.

E. Laricis OUD. — Stromatibus amphigenis, expositis, punctiformibus, nigris, catenas conidiorum longiusculas, in placentam convexam arete condensatas, gerentibus; conidiis primo angulatis, denique globulosis, continuis,  $5-6 \times 5 \mu$ , singulatim secedentibus, ferrugineis.

EXPLANATION OF THE PLATE.

Fig. A. Needle of *Larix decidua*; magnification 10 times; with the black spots of *Exosporina Laricis* OUD.

Fig. B. Hyphae or ribbons, extending over the leaf and in various places grown out to small-celled little disks, from which later the conidia, connected to strings, will arise Magn.  $\frac{200}{1}$ .

Fig. C. Ripe cushion of strings of conidia, as they would appear on a cross-section. Magn.  $\frac{500}{1}$ .

Fig. D. Part of such a cushion, enlarged  $\frac{1000}{1}$ . Each separate string shows a spherical top-cell.

Fig. E. CORDA'S picture of *Trimmatostroma Salicis*.

Fig. F. SACCARDO'S picture of *Exosporium fructicola*.

I am much indebted to Mr. C. J. KONING at Bussum, who has been kind enough to draw the plate for me.

**Mathematics.** — "PLÜCKER'S numbers of a curve in  $S_n$ " by Prof. P. H. SCHOUTE.

The PLÜCKER'S numbers of a curve in the space  $S_n$  with  $n$  dimensions have been given for the first time by VERONESE (*Math. Annalen*, vol. 19, page 195), yet they have been seldom applied although dating from 1882. This is probably due to the more or less awkward

notation which is made use of and which has been adopted i. a in PASCAL'S *Repertorium der höheren Mathematik* (Leipzig, Teubner, 1902). In the following lines I intend to give a more concise notation, making it possible to write down the  $3(n-1)$  relations between the  $3n$  PLÜCKER'S quantities in three formulae with an index, which must take the values  $1, 2, \dots, n-1$  successively. In order to make the deduction clear to those, who are not so familiar with polydimensional theories I shall begin by indicating them for the case  $n=3$  of our space.

2. As is known the six relations between the nine PLÜCKER'S quantities of a skew curve are derived in two triplets from the consideration of two plane curves, the first of which is the central projection of the given skew curve  $C$  from any point  $O$  on any plane  $\alpha$ , whilst the second is the section of any plane  $\alpha$  with the developable of the tangents to the curve  $C$ . Let us indicate successively order, rank, class of the curve  $C$  by  $n, r, m$  and let us represent as is customary by  $(a, b), (g, h), (x, y)$  the three pairs of dualistically related numbers, of which  $b$  is the number of stationary points,  $h$  the number of apparent nodes,  $x$  the order of the nodal curve of the developable; then the sextuples

$$(u_1, m_1, d_1, t_1, k_1, b_1) \quad , \quad (u_2, m_2, d_2, t_2, k_2, b_2)$$

of the quantities (order, class and numbers of nodes, double tangents, cusps and inflexions) characterizing the two plane curves are expressed by the equations

$$\left. \begin{array}{l} u_1 = n \\ m_1 = r \\ d_1 = h \\ t_1 = y \\ k_1 = b \\ b_1 = m \end{array} \right\} , \quad \left. \begin{array}{l} u_2 = r \\ m_2 = m \\ d_2 = x \\ t_2 = g \\ k_2 = n \\ b_2 = a \end{array} \right\} \dots \dots \dots (1)$$

in the nine characterizing values of  $C$ : so in connection with the well known PLÜCKER'S formulae for a plane curve the two triplets of relations hold good:

$$\left. \begin{array}{l} r = n(n-1) - 2h - 3b \\ n = r(r-1) - 2y - 3m \\ m - b = 3(r-n) \end{array} \right\} , \quad \left. \begin{array}{l} m = r(r-1) - 2x - 3n \\ r = m(m-1) - 2g - 3a \\ a - n = 3(m-r) \end{array} \right\} . (2)$$

If we substitute  $r_0, r_1, r_2, r_3, r_4$  for the row of quantities  $b, n, r, m, a$

and if we put  $d_1, t_1$  and  $d_2, t_2$  for  $h, y$  and  $x, y$  the equations (1) pass into

$$\left. \begin{aligned} n_i &= r_i \\ m_i &= r_{i-1} \\ k_i &= r_{i-1} \\ b_i &= r_{i+2} \end{aligned} \right\}, (i = 1, 2) \dots \dots \dots (1)$$

and identities, whilst the two triplets of equations (2) are united to

$$\left. \begin{aligned} r_{i+1} &= r_i(r_i - 1) - 2d_i - 3r_{i-1} \\ r_i &= r_{i+1}(r_{i+1} - 1) - 2t_i - 3r_{i+2} \\ r_{i+2} - r_{i-1} &= 3(r_{i+1} - r_i) \end{aligned} \right\}, (i = 1, 2) \dots \dots (2')$$

And now these equations pass into those for the general case as soon as the addition ( $i = 1, 2$ ) is exchanged for ( $i = 1, 2, \dots, n-1$ ).

3. We shall now pass to the general case of a curve  $C_n$  of order  $n'$ , lying in an  $S_n$  but not in an  $S_{n-1}$  and we remind the readers how here we determine the  $3(n-1)$  relations between the  $3n$  characterizing quantities. If we take in  $S_n$  two non-intersecting spaces  $S_i, S_{n-p-1}$ , and if we project  $C_n$  out of  $S_{i-p-1}$  on  $S_p$ , the projection is a curve  $C'_p$ . If we imagine this process to be performed for  $p = 2, 3, \dots, n-1$ , we arrive at — the curve  $C_n$  included — a series of  $n-1$  curves  $C_2, C_3, \dots, C_{n-1}, C_n$ . If furthermore  $C_2^{(p)}$  — once more for  $p = 2, 3, \dots, n-1$  — is the section of the locus of the spaces  $S_{p-1}$  through  $p$  successive points of the curve  $C_{p+1}$  with any plane lying in the space  $S_{p+1}$  of that curve, we arrive at, — if the plane curve  $C_2$  already found above is represented by  $C_2^{(1)}$  —,  $n-1$  plane curves  $C_2^{(1)}, C_2^{(2)}, \dots, C_2^{(n-1)}$  and these furnish  $n-1$  triplets of relations. If the sextuples  $(n_i, m_i, d_i, t_i, k_i, b_i)$ , ( $i = 1, 2, \dots, n-1$ ) represent the characterizing numbers of these plane curves the  $3(n-1)$  equations hold good:

$$\left. \begin{aligned} m_i &= n_i(n_i - 1) - 2d_i - 3k_i \\ n_i &= m_i(m_i - 1) - 2t_i - 3b_i \\ b_i - k_i &= 3(m_i - n_i) \end{aligned} \right\}, (i = 1, 2, \dots, n-1).$$

By representing the series of  $n+2$  quantities

$$\left. \begin{array}{cccccc} b & n' & r^{(1)}, r^{(2)}, \dots, r^{(n-2)} & m & a & \\ \text{number of} & & & & & \\ \text{stationary} & \text{order,} & n-2 & \text{numbers} & \text{class,} & \text{number of} \\ \text{points} & \left\{ \right. & & \text{of rank.} & & \text{stationary} \\ & & & & & \text{spaces } S_{n-1} \end{array} \right\}$$

of  $C_n$  by  $r_0, r_1, \dots, r_n, r_{n+1}$  we find the equations (1') extended from ( $i=1, 2$ ) to ( $i=1, 2, \dots, n-1$ ), which equations cause the above-mentioned  $3(n-1)$  equations to pass into the equations (2'), in the same way extended from ( $i=1, 2$ ) to ( $i=1, 2, \dots, n-1$ ).

4. According to this notation the system of the  $3n$  PLÜCKER'S numbers of  $C_n$  consists of three groups: a group of  $n+2$  quantities  $r$  (numbers of rank), a group of  $n-1$  quantities  $d$  (numbers of double points), a group of  $n-1$  quantities  $t$  (numbers of double tangents). We shall now indicate what is the exact signification of those quantities.

*Numbers of rank.* We consider  $r_0, r_p, r_{n-1}$  separately.

By  $r_0$  we understand the number of stationary points of  $C_n$  i.e. the number of the points through which  $n+1$  successive spaces  $S_{n-1}$  through  $n$  successive points of the curve pass.

For  $p=1, 2, \dots, n$  we find that  $r_p$  indicates how many spaces  $S_{p-1}$  through  $p$  successive points of  $C_n$  cut any space  $S_{n-p}$ ; of these numbers  $r_1$  is the order and  $r_n$  the class of  $C_n$ .

The number of stationary spaces  $S_{n-1}$  of  $C_n$ , i.e. the number of spaces  $S_{n-1}$  through  $n+1$  successive points of  $C_n$  is indicated by  $r_{n+1}$ .

*Numbers of double points.* The quantity  $d_p$  is the number of double points of the section  $C_2$  of the locus of the spaces  $S_{p-1}$  through  $p$  successive points of  $C_{p+1}$  with a plane situated in the space  $S_{p+1}$  of that curve. So by returning from the projection  $C_{p+1}$  to the given curve  $C_n$  we find the following: If we project the single infinite number of spaces  $S_{p-1}$  through  $p$  successive points of  $C_n$  out of any space  $S_{n-p-2}$  we find a single infinite number of spaces  $S_{n-2}$  and therefore a twofold infinite number of intersections  $S_{n-4}$  of two non-successive spaces  $S_{n-2}$ . The locus of those spaces  $S_{n-4}$  is a curved space with  $n-2$  dimensions, cut in a certain number of points by any plane. This number of points, at the same time the order of this curved space, is  $d_p$ .

*Numbers of double tangents.* The quantity  $t_p$  is the number of double tangents of  $C_2$ . By ascending from  $C_{p+1}$  to  $C_n$  we arrive at the following: By projecting the single infinite number of spaces  $S_p$  through  $p+1$  successive points of  $C_n$  out of any space  $S_{n-p-2}$ , we find a single infinite number of spaces  $S_{n-1}$  enveloping a curved space of  $n-1$  dimensions. The number of double tangents of any plane section of this envelope is  $t_p$ .

For the rest it is easy to see that the numbers  $d_p$  and  $t_{n-p}$  refer to quantities dualistically opposite in the space  $S_n$ .

5. By means of the simple form of the PLÜCKER'S formulae we are now enabled to show more clearly that really all curves  $C_2^{(p)}$  belong as they should to the same genus. For this we prove the equality of the genera  $g_i$  and  $g_{i+1}$  of  $C_2^{(i)}$  and  $C_2^{(i+1)}$ .

According to the relations (1') extended to  $C_n^i$  we have

$$2g_i = (n_i - 1)(n_i - 2) - 2(d_i + k_i) = (r_i - 1)(r_i - 2) - 2(d_i + r_{i-1})$$

and therefore

$$2(g_{i+1} - g_i) = (r_{i+1}^2 - r_i^2) - 2(d_{i+1} - d_i) - 3(r_{i+1} - r_i) - 2(r_i - r_{i-1}). \quad (3)$$

Moreover the first of the three equations (2') for  $i$  and  $i + 1$  gives by means of subtraction

$$r_{i+2} - r_{i+1} = (r_{i+1}^2 - r_i^2) - 2(d_{i+1} - d_i) - (r_{i+1} - r_i) - 3(r_i - r_{i-1}). \quad (4)$$

Thus by subtraction of (4) from (3) we get

$$\begin{aligned} 2(g_{i+1} - g_i) &= (r_{i+2} - r_{i+1}) - 2(r_{i+1} - r_i) + (r_i - r_{i-1}) \\ &= (r_{i+2} - r_{i+1}) - 3(r_{i+1} - r_i) \end{aligned}$$

and from this equation the second member disappears in consequence of the third of the equations (2').

Let us observe by the way that the numbers of rank  $r_0, r_1, r_2, \dots, r_{n+1}$  of  $C_n$  form the first terms of a recurrent series with the third of the equations (2') as equation of condition and thus — for  $x$  as the variable — with  $(1-x)^3$  as denominator of the generating fraction.

In order to cause the representation to remain as simple as possible we have supposed the curve  $C_n$  to lack all higher singularities. For the influence of the latter we refer to the above-mentioned essay of VERONESE.

The PLÜCKER'S formulae given here shall be applied elsewhere to the case of the curve  $C_n$  of order  $2^{n-1}$  forming in  $S_n$  the section of  $n-1$  quadratic spaces  $Q_n^2$ .

**Mathematics.** — “On systems of conics belonging to involutions on rational curves.” By Prof. JAN DE VRIES.

1. We suppose the points of a rational plane curve  $C^n$  to be arranged in the groups of an involution  $I^s, s > 5$ , and bring a conic  $C^2$  through each quintuple of points belonging to a selfsame group. The system  $[C^2]$  formed in this way has evidently no double right lines, so that  $\eta = 0$ . So between the characterizing numbers  $\mu, r, \sigma$  exist the relations  $2r = \mu + \sigma$  and  $2\mu = r$ : so we have  $\sigma = 2\mu$  and  $r = 3\mu$ .

The numbers of pairs of lines can be determined in the following way. Let  $P, P', P''$  be three points of the same group of the  $I^s$ ; we make  $P$  to correspond to each of the points  $S$  which the right line  $P'P''$  determines on  $C^n$ ; as to  $P$  belong  $\frac{1}{2}(s-1)(s-2)$  pairs  $P', P''$  each point  $P$  in the correspondence  $(P, S)$  is conjugate to  $(s-1)_2 \cdot (n-2)$  points  $S$ . The pencil of rays having  $S$  as vertex determines on  $C^n$  an  $I^{n-1}$  having  $(n-2)(s-1)$  pairs  $P', P''$  in common with  $I^s$ ; so to each point  $S$  correspond  $(n-2)(s-1)(s-2)$  points  $P$ . When now two conjugate points  $P, S$  coincide, three points  $P, P', P''$  lie in the same right line and each of those points is to be regarded as a coincidence of the correspondence  $(P, S)$ . So the number of these collinear triplets is  $(n-2)(s-1)_2$ . The bearer of such a triplet forms with the connecting line of two points belonging to the same group a pair of lines of  $[C^2]$ ; consequently

$$\sigma = (n-2)(s-1)_2(s-3)_2 = 6(n-2)(s-1)_4.$$

From this ensues again

$$\mu = 2(n-2)(s-1)_4 \text{ and } r = 4(n-2)(s-1)_4.$$

2. On each conic of the system  $[C^2]$  five points  $P$  are lying and  $(2n-5)$  points  $X$  more. Each point of  $C^n$  can be regarded as a point  $P$  and as a point  $X$ . Of the  $\mu$  conics through that point there are  $(s-1)_4$ , connecting  $P$  with four points  $P'$  belonging to the same group; the remaining  $(2n-5)(s-1)_4$  contain besides  $X$  a quintuple of points of the  $I^s$  and  $(2n-6)$  points  $X'$  more, which we shall adjoin to  $X$ . The points  $X, X'$  evidently form a symmetric correspondence with the characterizing number  $(2n-6)(2n-5)(s-1)_4$ . Each coincidence of  $(X, X')$  furnishes a conic of  $[C^2]$ , touching  $C^n$ .

Besides these  $2(2n-6)(2n-5)(s-1)_4$  conics there is a group of touching conics each of which connects a coincidence of  $I^s$  with three points belonging to the same group of  $I^s$ ; their number amounts to  $2(s-1)(s-2)_3 = 8(s-1)_4$ .

But there is still a third group of tangential conics. When a point  $P$  coincides with one of the points  $X$ , the conic touching  $C^n$  in  $P, X$  represents two curves; so in that point  $C^n$  touches likewise the envelope of  $[C^2]$ . Now to each point  $P$  belong  $(2n-5)(s-1)_4$  points  $X$ , whilst each point  $X$  is conjugate to  $5(2n-5)(s-1)_4$  points  $P$ . Therefore the third group contains  $6(2n-5)(s-1)_4$  conics. By counting these double we arrive at

$[2(2n-6)(2n-5) + 8 + 12(2n-5)](s-1)_4$  or  $4(n-2)(2n-1)(s-1)_4$  conics touching  $C^n$ . This number can be easily controlled; for, a curve  $C^k$  of class  $k$ , is touched by  $(k\mu + nr)$  curves of a system

$(\mu, r)$ . If for  $k$  we substitute here  $2(n-1)$  and for  $\mu, r$  the above-mentioned numbers, the number  $4(n-2)(2n-1)(s-1)_4$  appears again.

3. Let us still consider the correspondence between a point  $X$  and a point  $P_0$  belonging to the group of  $I^s$ , five points of which lie with  $X$  on a  $C^2$ . Each point  $X$  is conjugate to  $(2n-5)(s-1)_4 \cdot (s-5)$  points  $P_0$ ; reversely  $(s-1)_5 \cdot (2n-5)$  points  $X$  correspond to  $P_0$ . If two conjugate points coincide we have evidently a conic bearing six points belonging to a selfsame group of  $I^s$ . As each of those six points can be regarded as a point  $X$  the number of those conics is equal to the sixth part of the number of coincidences of the correspondence  $(P_0, X)$ , thus equal to  $(2n-5)(s-1)_5$ .

4. If every group of an  $I^s$  contains less than 5 points, there is no indicated system  $[C^2]$ . In that case we can take  $(5-s)$  arbitrary points  $A_k$ ,  $k=1$  to  $(5-s)$ , and join these by a  $C^2$  with the  $s$  points of a group of the  $I^s$ . To find the characterizing number  $\mu$  for the system  $[C^2]$  obtained in this way, we consider the conics passing through the points  $A_k$  and moreover through the arbitrary point  $A_0$ .

They intersect  $C^n$  in the groups of an involution  $I_{s-1}$  of order  $2n$  and rank  $(s-1)$ . Now two involutions  $I_{k_1}^{n_1}$  and  $I_{k_2}^{n_2}$  have according to a theorem of LE PAIGE <sup>1)</sup>,  $(n_1-k_1)_{k_2}(n_2-k_2)_{k_1}$  groups of  $(k_1+k_2)$  points in common. Applying this to the involutions  $I_{s-1}^{2n}$  and  $I_1^s$ , we find that through  $A_0$  pass  $(2n-s+1)$  conics containing each a group of the  $I^s$ . So  $\mu = (2n-s+1)$ ,  $r = 2(2n-s+1)$  and  $\sigma = 3(2n-s+1)$ .

5. For  $s=2$  three fixed points  $A_1, A_2, A_3$  are wanted. The pairs of lines of  $[C^2]$  form two groups. A figure of the first group consists of a right line  $A_k A_l$  and the line connecting  $A_m$  with the point which forms with one of the  $n$  points of intersection of  $C^n$  and  $A_k A_l$  a pair of the  $I^2$ . In a figure of the second group the line containing a point  $A_m$  bears a pair of the  $I^2$ . The number of pairs situated on rays through  $A_m$  amounts to  $(n-1)$ . So we find  $\sigma = 3n + 3(n-1) = 3(2n-1)$ , in correspondence with the general result given above.

For  $s=3$  we have to take two fixed points  $A_1, A_2$ . The pairs of lines form three groups. In the first place there are  $(n-3)$  collinear triplets (see § 1), of which the bearers through  $A_1, A_2$  are completed to a pair of lines; secondly each point of intersection of

<sup>1)</sup> Sur le nombre des groupes communs à des involutions supérieures, marquées sur un même support (Bull. de l'Acad. Royale de Belgique, 3e série, t. XI, p. 121).

$A_1 A_2$  with  $C^n$  determines a group of the  $I^3$  of which the remaining two points furnish the second right line of the degenerated  $C^2$ : thirdly each of the points  $A_1, A_2$  is collinear with  $2(n-1)$  pairs of the  $I^3$ . So we have  $d = n - 2 + n + 4(n-1) = 6(n-1)$ .

For  $s = 4$  we want but one fixed point  $A_1$ . There are  $3(n-2)$  collinear triplets and  $3(n-1)$  pairs of lines, where each of the right lines bears two points of a group of  $I^4$ : so here we find  $d = 3(n-2) + 3(n-1) = 3(2n-3)$ .

6. The correspondence  $(X, X')$  has for  $s < 5$  the characterizing number  $(2n-s)(2n-s-1)$ : in the correspondence  $(P, X)$  each point  $P$  is conjugate to  $(2n-s)$  points  $X$ , each point  $X$  to  $s(2n-s)$  points  $P$ . As  $I^s$  contains  $2(s-1)$  coincidences the number of conics of  $[C^2]$  touching  $C^n$  is now represented by  $2(2n-s)(2n-s-1) + 2(2n-s)(s+1) + 2(s-1) = 2(2n-1)(2n-s+1)$ , which corresponds to the value the number  $(ku + nr)$  possesses here.

The correspondence  $(X, X')$  for an  $I^2$  is of order  $(2n-2)(2n-3)$ : it has  $(2n-2)(2n-3)$  pairs in common with  $I^2$ .

So the system  $[C^2]$  contains  $(n-1)(2n-3)$  conics bearing each two pairs of the quadratic involution.

**Mathematics.** — “*Fundamental involutions on rational curves of order five*” by Prof. JAN DE VRIES.

1. If the points of a rational curve of order five,  $C^5$ , with six double points  $D_k$  ( $k = 1, 2, 3, 4, 5, 6$ ), are arranged in the pairs  $P', P''$  of an involution  $I^2$ , the line  $P'P''$  envelopes a directing curve of class four. For, the indicated involution has four pairs in common with the central involution of order five, which is determined by the rays of a pencil. If a pair of the  $I^2$  is formed by the points  $D'_6$  and  $D''_6$  lying in  $D_6$  on the two branches of the  $C^5$ , the directing curve breaks up into a curve of class three and the pencil of rays having its vertex in  $D_6$ . If a second pair consists of the points  $D'_5$  and  $D''_5$ , the real directing curve will be a conic. Then we evidently get an  $I^2$  given with  $C^5$ ; we shall therefore call it a *fundamental* involution. It is determined by the pencil of conics with the base-points  $D_1, D_2, D_3, D_4$ .

2. The bearer of a pair of points of the fundamental involution  $P'_{56}$  meets  $C^5$  in three points more  $T', T'', T'''$  forming a group of a cubic involution. For, of the tangents out of a point  $T' \equiv P'$

of the  $C^5$  one goes to point  $P''$ , whilst the second contains a pair of the  $F_{5,6}^2$  besides the points  $T''$ ,  $T'''$  conjugate to  $T'$ , so that  $T'$  appears in but *one* group of the correspondence  $(T', T'')$ . So the directing conic  $\varphi_{5,6}^2$  is at the same time the directing curve for the fundamental involution  $F_{5,6}^3$  composed of linear triplets  $T'$ ,  $T''$ ,  $T'''$ .

The tangents out of a point  $P'$  of the  $C^5$  to  $\varphi_{5,6}^2$  will coincide only in the case that  $P''$  is situated on the tangent in  $P'$  to  $C^5$ . From this follows that  $\varphi_{5,6}^2$  touches the curve  $C^5$  in five points; it is easy to see that these points are the coincidences of the correspondence (2, 3) in which a point  $P$  corresponds to a point  $T$ . Besides the tangents in these points to be counted double  $C^5$  and  $\varphi_{5,6}^2$  have six tangents more in common, which are determined by the coincidences of  $F_{5,6}^2$  and  $F_{5,6}^3$ .

3. The cubic curves connecting three triplets of the  $F_{5,6}^3$  with the six points  $D_k$  determine a pencil of curves determining the groups of this involution. A pair of the  $F_{5,6}^3$  consisting of the points  $D_5$ ,  $D'_5$ , the cubic pencil  $(C^{(3)})$  will contain a curve having in  $D_5$  a node; but from this follows that the remaining curves must touch each other in  $D_5$ , so also in  $D_6$ . The triplet of the  $F_{5,6}^3$ , of which the bearer  $t_6$  passes through  $D_6$  determines in the pencil  $(C^{(3)})$  a degenerated curve consisting of  $t_6$  and the conic  $k_{12345}^2$  through the points  $D_k$  ( $k = 1, 2, 3, 4, 5$ ). A second degenerated curve consists of the conic  $k_{12346}^2$  and a ray  $t_5$  through  $D_5$ . From this ensues that the ninth base-point of  $(C^{(3)})$  lies in the point of intersection of  $t_5$  and  $t_6$  whilst  $k_{12345}^2$  is touched in  $D_5$  by  $t_5$  and  $k_{12346}^2$  in  $D_6$  by  $t_6$ ; it goes without saying that in  $D_5$  and  $D_6$  all curves of  $(C^{(3)})$  have the lines  $t_5$  and  $t_6$  as tangents.

4. We consider the two fundamental involutions  $F_{4,6}^2$  and  $F_{5,6}^2$ , besides the involutions  $F_{4,6}^3$  and  $F_{5,6}^3$  determined by them and we inquire after the meaning of the common tangents of the directing conics  $\varphi_{4,6}^2$  and  $\varphi_{5,6}^2$ .

The involutions  $F_{4,6}^3$  and  $F_{5,6}^3$  have besides the pair of points  $D_6$ ,

$D''_6$ , a pair in common which we shall indicate by  $P'_{16}$ ,  $P''_{16}$  and also by  $T''_{56}$ ,  $T'''_{56}$ . On the connecting line  $r$  of these points are also the points  $T'_{46}$ ,  $T''_{46}$ ,  $T'''_{46}$ , which can just as well be indicated by the symbols  $T''''_{56}$ ,  $P'_{56}$ ,  $P''_{56}$ ; consequently  $r$  bears also the pair which  $F''_{56}$  and  $F^3_{46}$  have in common (besides  $D'_6$ ,  $D''_6$ ).

The involutions  $F^3_{46}$  and  $F''_{56}$  have four pairs in common among which the pair  $D'_6$ ,  $D''_6$ ; the remaining three lie on three common tangents of  $\mathcal{G}_{46}$  and  $\mathcal{G}_{56}$ ; the fourth common tangent is evidently the above mentioned right line  $r$ .

5. Let  $S_{kl}$  be the point of intersection of  $U^5$  with the right line  $D_k D_l$ . From the preceding ensues that the lines  $S_{12} S_{34}$ ,  $S_{13} S_{24}$  and  $S_{14} S_{23}$  determine with the lines  $t_5$ ,  $t_6$  touching the conics  $k_{12345}$ ,  $k_{12346}$  in  $D_5$ ,  $D_6$  a conic  $\mathcal{G}_{56}^2$  touching  $U^5$  five times.

Besides the fifteen pairs of fundamental involutions  $F^2_{kl}$ ,  $F^3_{kl}$  we still notice the 6 central fundamental cubic involutions intersected by the pencils of rays with vertices  $D_k$ . For these the directing curve (being for a general  $I^3$  of class 8) breaks up into the vertex to be counted three times and the remaining five points  $D$ .

**Physics.** — “*The determination of the pressure with a closed airmanometer.* By C. H. BRINKMAN. (Communicated by Prof. J. D. VAN DER WAALS).

For the determination of the pressure with the aid of closed airmanometers we may avail ourselves of AMAGAT's wellknown determinations of isotherms<sup>1)</sup>. In table 5 and 10 (l.c.) four air isotherms are given for pressures ranging between 100 à 3000 ats. For pressures, smaller than 100 ats. we have to extrapolate. I have thought that I could justly avail myself for this extrapolation of the equation of state of VAN DER WAALS:

$$p = \frac{(1+a)(1-b_1)(1+at)}{v-b} - \frac{a}{v^2}$$

if  $b$  is taken here as a function of the volume.

The variability of  $b$  with the volume has been interpreted in two ways: 1<sup>st</sup>. as a quasi change in consequence of the partial coinci-

1) Mémoires sur l'élasticité et la dilatabilité des fluides jusqu'aux très hautes pressions. Ann. Ch. Phys. 6e s. 1893.

dence of the distance spheres, 2<sup>nd</sup> as a real change caused by compression<sup>1)</sup>.

At first I thought that I had to make use of the formula, derived by Prof. VAN DER WAALS on the second supposition with the aid of the theory of cyclic motion: when testing this formula to the hydrogen isotherms of AMAGAT, VAN LAAR<sup>2)</sup>, found it to harmonize well with the observations. In the calculation we are, however, confronted with the difficulty that for the accurate determination of the constants  $b_g$  and  $b_o$  a preliminary accurate knowledge of the  $a$  is required. It not having been ascertained to which of the two causes the variability of the  $b$  is due, and it being improbable, that the first mentioned cause can be left out of consideration, I have used the formula derived on the first supposition for the variability of the  $b$ :

$$b = b_g \left\{ 1 - \alpha \frac{b_g}{v} + \beta \frac{b_g^2}{v^2} - \gamma \frac{b_g^3}{v^3} + \dots \right\}$$

Of the eleven correction terms which will occur for spherical molecules<sup>3)</sup>, only the first two have been calculated. I have confined myself here to three terms. By a comparison with the values of  $\mu$  and  $v$  observed by AMAGAT at 15,<sup>67</sup> C. we shall have to determine the values of  $\alpha$ ,  $b_g$ ,  $\beta$  and  $\gamma$  which agree closest with the observations between 100 and 3000 ats. In order to avoid when applying the method of least squares, the elaborate calculation of five normal equations with twenty coefficients, I have determined the most probable values of  $\alpha$  and  $b_g$  with the aid of assumed values of  $\beta$  and  $\gamma$ . For this purpose I put  $\alpha = \frac{3}{8}$ , which value was found according to two different methods by BOLTZMANN<sup>4)</sup> and by VAN DER WAALS JUN.<sup>5)</sup>; further  $\beta = 0,0958$ , which value has been calculated by VAN LAAR<sup>3)</sup> and adopted<sup>6)</sup> by BOLTZMANN; quite arbitrarily I put  $\gamma = 0,01$  and I assumed as approximated values of  $\alpha$  and  $b_g$   $\alpha = 0,0028$   $b_g = 0,0020$ <sup>7)</sup>. So if  $\Delta \alpha$  and  $\Delta b_g$  are the differences between the

1) See VAN DER WAALS, These Proc. V. June 27 1903, p. 123.

BOLTZMANN Festschrift p. 305.

2) These Proc. V. March 28, 1903 p. 573.

3) VAN LAAR, Evaluation de la deuxième correction sur la grandeur  $b$ , Arch. Teyler, série II, t. VI 1899 p. 48.

4) Gastheorie II p. 152.

5) These Proc. V. February 28 1903 p. 487.

6) These Proc. I March 25, 1899, p. 398. Adopted namely for the calculation of his second correction term, which has the value

$$\beta' = \frac{3\beta}{2} = \frac{957}{8960}$$

Here  $\beta$  has the value 0,0958 calculated by VAN LAAR so  $\beta' = 0,0369$ . (Febr. 24, 1904).

7) In Cont. I  $\alpha = 0,0037$ ,  $b = 0,0026$  is derived from the observations of REGNAULT. When multiplied with 0,76 with change of the unity of pressure, the above values are obtained.

most probable and the assumed values of  $a$  and  $b_g$ ,  $\Delta p$  the difference between the observed pressure and that calculated with the aid of the five assumed constants, the normal equations become:

$$\begin{aligned} \Delta a \cdot \sum \left\{ \frac{\partial p}{\partial a} \right\}^2 + \Delta b_g \cdot \sum \left\{ \frac{\partial p}{\partial a} \cdot \frac{\partial p}{\partial b_g} \right\} &= \sum \Delta p \cdot \frac{\partial p}{\partial a} \\ \Delta a \cdot \sum \left\{ \frac{\partial p}{\partial a} \cdot \frac{\partial p}{\partial b_g} \right\} + \Delta b_g \cdot \sum \left\{ \frac{\partial p}{\partial b_g} \right\}^2 &= \sum \Delta p \cdot \frac{\partial p}{\partial b_g} \end{aligned}$$

By solving them for seven observations between 100 and 400 ats. (where the influence of the arbitrary values  $\gamma$ ,  $\beta$  and  $a$  is not yet very great), we find:  $a = 2410$ ;  $b_g = 1906$ <sup>1)</sup>.

In the third column of table I the difference between the observed values of  $p$  and those calculated with these new values of  $a$  and  $b_g$  have been given in per cents of  $p$ ; the agreement is satisfactory up to 1000 ats. In order to find values of  $a$ ,  $\beta$  and  $\gamma$ , which give a better agreement for higher pressures, I have calculated the  $b$  for volumes 3209, 2060, 1643 and 1466 (with corresponding pressures of 400, 1000, 2000 and 3000 ats.<sup>2)</sup>) from the equation of state with the aid of the just found  $a$ . Let us now write the correction formula of the  $b$  in this form:

$$b \cdot \frac{1}{b_g} + \frac{1}{v} \cdot a \cdot b_g - \frac{1}{v^2} \cdot \beta \cdot b_g^2 + \frac{1}{v^3} \cdot \gamma \cdot b_g^3 = 1$$

Then with the aid of those four sets of values of  $b$  and  $v$  we may calculate from four linear equations with four unknown quantities a  $b_g$ ,  $a$ ,  $\beta$  and  $\gamma$ , which with  $a = 2410$  for volumes 3209, 2060, 1643 and 1466 yield values for  $p$ , which agree perfectly with the observed values. We find  $b_g = 1863$ ,  $a = 0,3616$ ,  $\beta = 0,1330$ ,  $\gamma = 0,05176$ ; with the aid of these values of  $a$ ,  $\beta$  and  $\gamma$  we find now the values of  $a$  and  $b_g$  which give the best agreement with the observation, by applying the two normal equations to ten observations between 100 and 1000 ats. The values found in this way and the deviations of  $p$  calculated by means of them are given in the fourth column of table I: now the agreement is satisfactory up to 2000 ats. Only by changing  $\beta$  and  $\gamma$  we can obtain a better agreement for the highest pressures. New values of  $\beta$  and  $\gamma$  are now found from the correction formula for the  $b$  with the aid of the just found values of  $a$ ,  $b_g$  and  $a$ , and these new values make the agreement at 2000 and 3000 ats. satisfactory.

<sup>1)</sup> The values given for  $a$ ,  $b$  and  $v$  must be multiplied with  $10^{-6}$ .

<sup>2)</sup> The values of  $p$ , given by AMAGAT for different values of  $v$ , have been borrowed up to 1000 ats. from his "methode des regards", those from 1000 to 3000 ats. from his "methode des contracts électriques".

T A B L E I.

$a$	2410	2358.6	2358.6
$b_p$	4906	4852.0	4852.0
$z$	0.375	0.3616	0.3616
$\varepsilon$	0.0958	0.1330	0.1325
$\gamma$	0.01	0.05176	0.05083

$v$	$p(15^\circ, 7)$ (observed)	$\Delta F$	$\Delta P$	$\Delta P$
10430	100	0.1	0.2	0.2
5427	200	-0.1	0.0	0.0
3913	300	0.1	0.2	0.2
3209	400	-0.2	-0.2	-0.2
2822	500	0.4	0.2	0.2
2060	1000	-0.2	0.1	0.0
1793	1500	-2.2	0.6	0.4
1643	2000	-6.4	0.8	0.3
1542	2500	-12.5	0.9	0.2
1466	3000	-21.1	1.0	0.0

These values and the deviations of  $p$  calculated with them are given in the fifth column of table I. The deviations are of the same order as those which Prof. KAMERLINGH ONNES<sup>1)</sup> obtains when representing AMAGAT's observations by an equation of state with six constants in the form of a series.

A reliable extrapolation for pressures below 100 atms. has now become possible: at a temperature of  $15^\circ, 7$  C. the pressure corresponding to every volume can be determined with the aid of the five constants.

If the air-manometer is placed in a water bath, the temperature of which is kept constant by a thermo-regulator, a temperature of  $20^\circ$  or  $25^\circ$  will be preferred to  $15^\circ, 7$  C. It is therefore of importance to ascertain, whether also at those higher temperatures the equation of state with the same five constants yields values which sufficiently harmonize with AMAGAT's observations. It is to be expected that this will only be possible within a limited range of temperatures:

1) These Proc. IV June 29, 1901. p. 125.

for the quantity  $\frac{\partial p}{\partial t_v}$  derived by AMAGAT from the isotherm is not constant, which points to the fact that by assuming the constants independent of the temperature, no perfect agreement with the observations will be obtained.

By means of the formula:

$$\frac{\partial p}{\partial t_v} = \frac{(1+a)(1-b_1) \cdot a}{v-b}$$

which is derived from the equation of state, when the constants are put independent of the temperature, I have determined the  $\frac{\partial p}{\partial t}$  for different volumes, and compared these values with those found by AMAGAT.†)

T A B L E II.

$v$	$t$ (°C) (observed)	$\frac{\partial p}{\partial t_v}$ (0°-100°) (observed)	$\frac{\partial p}{\partial t_v}$ (calculated)	$\Delta$
9730	100	0.462	0.458	0.9
5050	200	1.405	1.673	2.9
3658	300	1.800	1.750	2.8
3036	400	2.470	2.407	2.5
2680	500	3.085	3.042	1.4
2450	600	3.718	3.648	1.9

In the third column of table II the values of  $\frac{\partial p}{\partial t_v}$  are given derived by AMAGAT from his determination of isotherms at 0° and at 100°, in the fourth column the calculated values, and in the fifth the deviations expressed in per cents of  $\frac{\partial p}{\partial t_v}$ .

If by means of the formula for  $\frac{\partial p}{\partial t_v}$  we calculate from the pressure at 15°, the pressure at 25°, then the deviation of 0,9 % in the  $\frac{\partial p}{\partial t_v}$  passes into one of 0,04 % in the pressure for the volume 9730. The deviation of the  $p$  introduced in this way, is smaller than

†) l. c. Table 26.

those which are mentioned at 15°,7 in table I; from which follows that the accuracy of the values of  $p$  at 25° derived from the equation of state is still of the same order as those which are calculated at 15°.7.

In table III the values of  $p$  are given at temperatures of 15°,7, 20° and 25° C. for different volumes calculated from the equation of state with the constants mentioned in the fifth column of table I. In order to render the calculation of pressures possible also for other temperatures, the calculated values of  $\frac{\partial p}{\partial t_v}$  are mentioned in the fifth column of table III. (p. 516).

As unit of volume we have taken the normal volume, i. e. the volume which the air would occupy at 0° C. and 1 atm. (0°, 45° N. B.).

So it is possible to represent an isotherm for a large range of densities, with the aid of the equation of state and values for the constants  $\alpha$  and  $\beta$ , differing little from the theoretical values.

These differences will be chiefly determined, besides by systematic errors of the observations, by 1<sup>st</sup>. the non-spherical shape of bi-atomic molecules, 2<sup>nd</sup> the possibility of a simultaneous real diminution, which could then explain at the same time the slight variability of  $\frac{\partial p}{\partial t_v}$ .

In table V the influence for different densities of the three terms of the correction formula for the  $b$  is rendered. In the fourth, fifth and sixth column the values are given, with which the  $b_g$  is diminished in consequence of the correction terms with  $\alpha$ ,  $\beta$  and  $\gamma$ , expressed in per cents of  $b_g$ ; in the seventh column the decrease of  $b_g$  in consequence of the three terms together is given in per cents of  $b_g$ . In the eighth column the influence of the decrease of  $b_g$  on the pressure is represented; if we calculate the  $p$  from the equation of state keeping  $b$  constant and equal to  $b_g$ , then this  $p$  will be greater than that calculated by means of the decreasing  $b$ .

The difference between them is given in per cents of  $p$ . With a volume of 0,02 already the decrease of  $b$  will manifest itself in a decrease of  $p$ .

It appears that the application of several correction terms would be desirable for the smallest of the volumes observed by AMAGAT. For larger volumes, however, they have no influence, and their theoretical values still being unknown, I have thought that in this case three terms would be sufficient.

Several observers (i. a. KUENEN, QUINT) have made use of the air-isotherm, determined by AMAGAT as early as 1864, for pressures

T A B L E III<sup>1)</sup>.

$\frac{1}{v}$	$p(15^{\circ}.7)$	$p(20^{\circ})$	$p(25^{\circ})$	$\frac{\partial p}{\partial t_r}$
5	5.28	5.56	5.45	0.018
10	10.54	10.70	10.89	0.037
15	15.79	16.03	16.32	0.057
20	21.02	21.35	21.73	0.076
25	26.24	26.66	27.14	0.096
30	31.45	31.95	32.53	0.116
35	36.65	37.23	37.92	0.137
40	41.84	42.52	43.31	0.158
45	47.02	47.79	48.69	0.179
50	52.21	53.07	54.08	0.201
55	57.40	58.36	59.48	0.224
60	62.58	63.64	64.87	0.246
65	67.78	68.94	70.28	0.269
70	72.97	74.23	75.69	0.293
75	78.18	79.54	81.13	0.317
80	83.39	84.86	86.57	0.341
85	88.63	90.20	92.03	0.366
90	93.88	95.56	97.52	0.391
95	99.15	100.95	103.03	0.417
100	104.44	106.34	108.56	0.443
105	109.76	111.78	114.13	0.470
110	115.10	117.24	119.73	0.497
115	120.47	122.73	125.36	0.525
120	125.81	128.27	131.04	0.554
125	131.33	133.84	136.75	0.583
130	136.82	139.46	142.52	0.612
135	142.36	145.12	148.33	0.642
140	147.91	150.80	154.17	0.672
145	153.53	156.55	160.07	0.703
150	159.21	162.38	166.05	0.735

<sup>1)</sup> The error of calculation, made in the  $p$  by interpolating linearly for intermediate volumes, is smaller than 0.01 atm.

T A B L E IV.

$v$	$p(15^{\circ}.7)$	$\frac{b_g}{v}$	$\frac{\alpha b_g^2}{v}$	$\frac{\beta b_g^3}{v^2}$	$\frac{\gamma b_g^4}{v^3}$	$b_g - b$	$\Delta p$
100000	10.54	0.02	0.67	-0.00	0.00	0.67	0.0
20000	52.21	0.09	3.35	-0.11	0.00	3.24	0.4
10000	104.4	0.19	6.70	-0.45	0.03	6.28	2
4504	249.5	0.41	14.87	-2.24	0.35	12.98	16
2822	499.1	0.66	23.73	-5.71	1.44	19.46	59
2060	999.9	0.90	32.51	-10.71	3.69	25.49	353
1643	1994	1.13	40.76	-16.84	7.28	31.20	
1466	3000	1.26	45.68	-21.15	10.25	34.78	

between 25 and 85 atms., and a temperature of  $16^{\circ}$  C. As unit of volume the volume at  $16^{\circ}$  C. and 1 atm. has been used; so in order to be able to compare these results with those found later, all the observed volumes must be multiplied with 1,05873, and we can also calculate the pressure at  $15^{\circ}.7$  from the pressure at  $16^{\circ}$  with the aid of the  $\frac{\partial p}{\partial t_v}$  calculated before.

It appears in the graphical representation of  $p v$  as function of  $\frac{1}{v}$ , that the last series of observations, starting with 100 atms., can by no means be considered as a continuation of the former series which ends at 85 atms., so that it is impossible to use the two series together.

In the second column of table V the results of the measurements in 1864<sup>1)</sup> are given, reduced to  $15^{\circ}.7$  C. and to the normal volume as unit of volume; in the third column those which have been extrapolated in the way described above from the observations of 1893; in the fourth column the differences have been given in percents.

For the following reasons the later measurements seem more accurate to me. 1<sup>st</sup> The differences between two series of determinations found in the later measurements ("méthode des regards" and "méthode des contacts") amount to at the utmost 0,1% at  $15^{\circ}.7$ . 2<sup>nd</sup> The manometers of DESGOFFE used in these determinations have been compared and the deviations are not great, specially for high pres-

¶ l. c. Table II.

T A B L E V.

$\tau$	$p$ (15°.7)		$\Delta p$
	1864	1893	
39820	26.29	26.36	0.27
31790	32.85	32.96	0.33
26440	39.43	39.58	0.37
22610	46.00	46.22	0.48
19760	52.57	52.84	0.51
17550	59.14	59.45	0.53
15790	65.71	66.04	0.50
14340	72.28	72.69	0.56
13140	78.85	79.33	0.61
12140	85.42	85.88	0.53

tures, whereas the determination of the pressure in 1864 with an open manometer 65 meters high has been very difficult. 3<sup>rd</sup> Comparison of the accurate hydrogen isotherm of SCHALKWIJK (Diss. 1902) with the values extrapolated from AMAGAT's determinations gives differences of about 0,1 %.

**Chemistry.** — “On the shape of meltingpoint-curves for binary mixtures, when the latent heat required for the mixing is very small or = 0 in the two phases.” (3<sup>rd</sup> communication). By J. J. VAN LAAR. Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.

I. By the side of the *ideal* case, that the latent heat of mixing in the liquid phase = 0, whereas it is  $\infty$  in the solid phase ( $a = 0, a' = \infty$ ) — so that the solid phase consists only of one component — there is another case, also *ideal*, viz. that the latent heat of mixing = 0 in both phases, or may be neglected. ( $a=0, a'=0$ ). The solid phase consists then of the two components in a proportion which is comparable to that in the liquid phase.

The former ideal case is that of the processes of solidification, in which *no* solid solutions (or mixed crystals) are found, the latter may be appropriately called the ideal case of the *mixed crystals*.

To consider such ideal cases has always this use — apart from

the simplifications in the considerations and calculations — that these cases may be adopted as the *normal* ones, from which all the other cases are to be considered as deviations in greater or smaller degree.

In our case the consideration of the limiting case  $\alpha = 0$ ,  $\alpha' = 0$  offers another advantage, viz. that much of what will be deduced in what follows, may be transferred with some restrictions to the *boilingpoint-lines* for *ideal* liquid and gaseous phases. For the thermodynamic relations of equilibrium agree perfectly, when the distinguishing feature between the two kinds of equilibrium, viz. the degree of the mutual influence of the two components in each of the phases has vanished. The difference consists only in this, that for the processes of melting the pure latent heat of melting may be assumed to be independent of the temperature, whereas for the processes of boiling the latent heat of evaporation will decrease with increasing temperature. Only in those cases, therefore, in which the boiling points of the two components do not differ much, the following considerations may be transferred to boilingpoint-curves of liquids, where  $\alpha$  may be put  $= 0$ . When the difference between the boiling points is larger, this cannot be done any more.

II. The fundamental equations (2) of my *first* paper<sup>1)</sup> become  $\left( \beta = \frac{\alpha}{q_1} = 0, \beta' = \frac{\alpha'}{q_1} = 0 \right)$  simply:

$$T = \frac{T_1}{1 + \frac{RT_1}{q_1} \log \frac{1-x'}{1-x}} = \frac{T_2}{1 + \frac{RT_2}{q_2} \log \frac{x'}{x}} \quad \dots \quad (1)$$

It is now possible to eliminate  $x'$ , and to express  $x$  explicitly in  $T$ , and in the same way to express the quantity  $x'$  explicitly in  $T'$  after eliminating  $x$ .

In the first place we find:

$$\frac{1-x'}{1-x} = e^{\frac{q_1}{R} \left( \frac{1}{T} - \frac{1}{T_1} \right)} \quad ; \quad \frac{x'}{x} = e^{-\frac{q_2}{R} \left( \frac{1}{T_2} - \frac{1}{T} \right)}, \dots \quad (2)$$

so that, when for shortness we put:

$$\frac{q_1}{R} \left( \frac{1}{T} - \frac{1}{T_1} \right) = \lambda_1 \quad ; \quad \frac{q_2}{R} \left( \frac{1}{T_2} - \frac{1}{T} \right) = \lambda_2, \dots \quad (3)$$

we get, in consequence of  $(1-x') + x' = 1$ , the relation:

$$(1-x)^{\lambda_1} + x^{\lambda_2} = 1.$$

<sup>1)</sup> These Proc. VI, June 27, 1903, p. 151.

In the same way:

$$(1-x')e^{-\lambda_1} + x'e^{\lambda_2} = 1.$$

From this we solve:

$$x = \frac{e^{\lambda_1} - 1}{e^{\lambda_1} - e^{-\lambda_2}} \quad ; \quad x' = \frac{e^{-\lambda_1} - 1}{e^{-\lambda_1} - e^{\lambda_2}}$$

or, in a form convenient for the calculation:

$$x' = \frac{e^{\lambda_1} - 1}{e^{\lambda_1 + \lambda_2} - 1} \quad ; \quad x = x' e^{\lambda_2} . . . . . (4)$$

From these equations, and also from equation (4) of the first communication (in which  $w_1 = q_1$  and  $w_2 = q_2$ ) we find easily:

$$\frac{dT}{dx} = - \frac{RT^2}{(1-x')q_1 + x'q_2} \cdot \frac{x-x'}{x(1-x)} \quad ; \quad \frac{dT}{dx'} = - \frac{RT^2}{(1-x)q_1 + xq_2} \cdot \frac{x-x'}{x'(1-x')}$$

For the *initial course* of the meltingpoint-curve follows from this ( $T = T_1$ ):

$$\left(\frac{dT}{dx}\right)_0 = - \frac{RT_1^2}{q_1} \left(1 - \left(\frac{x'}{x}\right)_0\right) \quad ; \quad \left(\frac{dT}{dx'}\right)_0 = - \frac{RT_1^2}{q_1} \left(\left(\frac{x}{x'}\right)_0 - 1\right),$$

or, in connection with (2):

$$\left(\frac{dT}{dx}\right)_0 = - \frac{RT_1^2}{q_1} (1 - e^{-\theta_2}) \quad ; \quad \left(\frac{dT}{dx'}\right)_0 = - \frac{RT_1^2}{q_1} (e^{\theta_2} - 1), \quad . . . (5)$$

when we put:

$$\frac{q_2}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \theta_2 . . . . . (6)$$

The *final course* (for the lowest temperature  $T_2$ ) is found by changing the letters, so, by putting further  $1-x=y$  and  $1-x'=y'$ :

$$\left(\frac{dT}{dy}\right)_0 = - \frac{RT_2^2}{q_2} \left(1 - \left(\frac{y'}{y}\right)_0\right) \quad ; \quad \left(\frac{dT}{dy'}\right)_0 = - \frac{RT_2^2}{q_2} \left(\left(\frac{y}{y'}\right)_0 - 1\right),$$

i.e. taking (2) into account:

$$\left(\frac{dT}{dy}\right)_0 = \frac{RT_2^2}{q_2} (e^{\theta_1} - 1) \quad ; \quad \left(\frac{dT}{dy'}\right)_0 = \frac{RT_2^2}{q_2} (1 - e^{-\theta_1}), . . . . . (5a)$$

when putting:

$$\frac{q_1}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \theta_1 . . . . . (6a)$$

$\theta_1$  and  $\theta_2$  being both *positive* quantities ( $T_2$  is always smaller than  $T_1$ ),  $e^{\theta_1}$  and  $e^{\theta_2}$  will always be  $> 1$ ,  $e^{-\theta_1}$  and  $e^{-\theta_2}$  always  $< 1$ .

From this follows, that the quantities  $\left(\frac{dT}{dx}\right)_0$  and  $\left(\frac{dT}{dx'}\right)_0$  will always

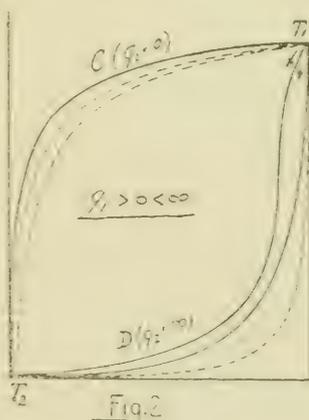
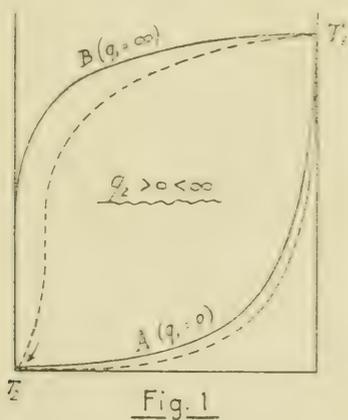
be *negative*, the quantities  $\left(\frac{dT'}{dy}\right)_0$  and  $\left(\frac{dT'}{dx}\right)_0$  always *positive*. For the latent heat of mixing  $q_1$  and  $q_2$  can never become negative.

So in the ideal case  $a = 0$ ,  $a' = 0$  the meltingpoint-curve always begins to *descend* at the *highest* temperature, and to *ascend* at the *lowest* temperature, so that in this case a minimum is excluded. This appears also from the fact that the condition for a minimum is  $\beta' > \frac{T_1 - T_2}{T_1}$  (loc. cit. p. 168), so that for  $\beta' = 0$  this can never occur, and the meltingpoint-curve will therefore gradually descend from  $T_1$  to  $T_2$ .

That a maximum cannot occur in *any* case for *normal* components, whatever value  $a$  or  $a'$  may have, — provided  $a'$  be larger than  $a$  — has been proved already in my first communication (loc. cit. p. 156).

The equations (5) and (5a) give rise to the following discussion.

In the limiting case  $q_1 = 0$  ( $q_2$  finite) we have  $\left(\frac{dT'}{dx}\right)_0 = -\infty$ ,  $\left(\frac{dT'}{dx'}\right)_0 = -\infty$ ,  $\left(\frac{dT'}{dy}\right)_0 = 0$ ,  $\left(\frac{dT'}{dy'}\right)_0 = 0$ , so that the two meltingpoint-curves will approach to the type *A* (fig.1).



For  $q_1 = \infty$ ,  $\left(\frac{dT'}{dx}\right)_0$  and  $\left(\frac{dT'}{dx'}\right)_0$  will approach to 0,  $\left(\frac{dT'}{dy}\right)_0$  to  $\infty$  (on account of the term  $e^{q_1}$ ), but  $\left(\frac{dT'}{dy'}\right)_0$  to a *limit*, viz.  $\frac{RT_2^2}{q_2}$ , as  $e^{-q_1}$  converges to 0. This gives the limiting-type *B* (fig.1).

When  $q_2 = 0$  ( $q_1$  finite) we have  $\left(\frac{dT'}{dx}\right)_0$  and  $\left(\frac{dT'}{dx'}\right)_0 = 0$ ;  $\left(\frac{dT'}{dy}\right)_0$

and  $\left(\frac{dT}{dy'}\right)_0 = \infty$ . The meltingpoint-curves approach to the type *C* (fig.2).

If, however,  $q_2 = \infty$ , then  $\left(\frac{dT}{dx}\right)_0 = -\frac{RT_1^2}{q_1}$ ,  $\left(\frac{dT}{dx'}\right)_0 = -\infty$ , and  $\left(\frac{dT}{dy}\right)_0$  and  $\left(\frac{dT}{dy'}\right)_0$  approach both to 0. Now  $\left(\frac{dT}{dx}\right)_0$  approaches to a limit, as  $e^{-\theta_2}$  converges to 0. This gives rise to the limiting-type *D* (fig.2).

We shall see presently, that according to  $q_1$  being greater or smaller, the final course for  $T=f(x')$  in the case *C*, and the initial course for  $T=f(x)$  in the case *D* may vary as to their curvature.

All the other cases lie between these extremes, but we shall see that there can yet be a great difference in course as to *concavity* and *convexity*. In order to form an opinion on this, however, we must write down the *second* differential-quotients.

III. We found for them in our *second* communication <sup>1)</sup> for  $T = T_1$ , when  $a$  and  $a' = 0$ :

$$\left(\frac{d^2T}{dx^2}\right)_0 = \frac{1}{q_1} \left(\frac{dT}{dx}\right)_0 \left[ (q_1 - 4T_1) - \left(\frac{x'}{x}\right)_0 \left\{ (q_1 - 4T_1) - 2(q_1 - q_2) \right\} \right] \quad (7)$$

$$\left(\frac{d^2T}{dx'^2}\right)_0 = \frac{1}{q_1} \left(\frac{dT}{dx'}\right)_0 \left[ (q_1 + 4T_1) - \left(\frac{x}{x'}\right)_0 \left\{ (q_1 + 4T_1) - 2(q_1 - q_2) \right\} \right]$$

in which  $\left(\frac{x'}{x}\right)_0$  is  $e^{-\theta_2}$  according to (2) and (6). For the corresponding expressions for  $T_2$  we find by the same changes as for  $\frac{dT}{dx}$  (see above):

$$\left(\frac{d^2T}{dy^2}\right)_0 = \frac{1}{q_2} \left(\frac{dT}{dy}\right)_0 \left[ (q_2 - 4T_2) - \left(\frac{y'}{y}\right)_0 \left\{ (q_2 - 4T_2) + 2(q_1 - q_2) \right\} \right] \quad (7a)$$

$$\left(\frac{d^2T}{dy'^2}\right)_0 = \frac{1}{q_2} \left(\frac{dT}{dy'}\right)_0 \left[ (q_2 + 4T_2) - \left(\frac{y}{y'}\right)_0 \left\{ (q_2 + 4T_2) - 2(q_1 - q_2) \right\} \right]$$

in which  $\left(\frac{y'}{y}\right)_0 = e^{\theta_1}$  according to (2) and (6a).

That these equations can give rise to a *point of inflection* in the meltingpoint-curve, so even at  $a' = 0$ , I have already proved in my *second* communication (loc. cit. p. 256—257).

<sup>1)</sup> These Proc. VI, Oct. 31, 1903, p. 256.

For a *concave beginning* (i. e. turned towards the X-axis)  $\frac{d^2T}{dx^2}$  is always negative (for  $\frac{dT}{dx}$  becomes larger negative). Hence  $\frac{d^2T}{dx^2} : \frac{dT}{dx}$  *positive*. On the other hand this quotient will be *negative* for a *convex beginning*. In the same way for  $T = f(x')$ .

With a *concave end*  $\frac{d^2T}{dy^2}$  will again be negative ( $\frac{dT}{dy}$  becomes smaller positive), so  $\frac{d^2T}{dy^2} : \frac{dT}{dy}$  *negative*. For a *convex end* this quantity will be *positive*. We have therefore the following transition conditions.

- I For  $T = f(x)$   $\left. \begin{array}{l} \text{concave} \\ \text{convex} \end{array} \right\} \begin{array}{l} \text{beginning } 2(q_1 - q_2) + (q_1 - 4T_1)(e^{\theta_2} - 1) > 0 \\ < 0 \end{array}$
- II For  $T = f(x)$   $\left. \begin{array}{l} \text{concave} \\ \text{convex} \end{array} \right\} \begin{array}{l} \text{end } -2(q_1 - q_2) - (q_2 - 4T_2)(1 - e^{-\theta_1}) < 0 \\ > 0 \end{array}$
- III For  $T = f(x')$   $\left. \begin{array}{l} \text{concave} \\ \text{convex} \end{array} \right\} \begin{array}{l} \text{beginning } 2(q_1 - q_2) - (q_1 + 4T_1)(1 - e^{-\theta_2}) > 0 \\ < 0 \end{array}$
- IV For  $T = f(x')$   $\left. \begin{array}{l} \text{concave} \\ \text{convex} \end{array} \right\} \begin{array}{l} \text{end } -2(q_1 - q_2) + (q_2 + 4T_2)(e^{\theta_1} - 1) < 0 \\ > 0 \end{array}$

or in another form :

$$\left. \begin{array}{l} \text{I } q_1 > 4T_1 + \frac{2(q_2 - 4T_1)}{1 + e^{\theta_2}} \\ \text{II } q_2 < 4T_2 + \frac{2(q_1 - 4T_2)}{1 + e^{-\theta_1}} \end{array} \right\} \left. \begin{array}{l} \text{III } q_1 < -4T_1 + \frac{2(q_2 + 4T_1)}{1 + e^{-\theta_2}} \\ \text{IV } q_2 > -4T_2 + \frac{2(q_1 + 4T_2)}{1 + e^{\theta_1}} \end{array} \right\} \quad (8)$$

The different regions with their limits, which occur in these conditions, are represented in fig. 3 (Plate). The figure holds for  $T_2 = \frac{1}{2} T_1$ , the values of  $q_1$  and  $q_2$  are expressed in multiples of  $T_1$ .

Let us subject the limiting-curves to a closer examination (see fig. 3).

a. *Curve I*, viz.

$$q_1 = 4T_1 + \frac{2(q_2 - 4T_1)}{1 + e^{\theta_2}} \dots \dots \dots (8I)$$

According to (8) all the curves  $T = f(x)$  with a *concave beginning* will lie *above* this curve, with a *convex beginning below* it. For  $q_1$  must then be respectively larger or smaller than the values given by the second member.

The curve will also yield  $q_1 = 0$  for  $q_2 = 0$ , for which  $e^{\theta_2} = 1$ . The *initial direction* is given by  $q_1 = q_2$  ( $45^\circ$ ). Further for  $q_2 = 4T_1$

is evidently also  $q_1 = 4T_1$ , and for  $q_2 = \infty$ ,  $e^{\theta_2}$  becoming  $= \infty$ ,  $q_1$  will again be  $4T_1$ . The curve I will therefore run pretty rapidly *asymptotically* to the straight line  $q_1 = 4T_1$  for higher values of  $q_2$ , and will show a *maximum* somewhere past  $q_2 = 4T_1$ . ( $M_1$  in fig. 3).

This maximum is represented by  $\left(\frac{dq_1}{dq_2} = 0\right)$ :

$$(1 + e^{\theta_2}) - (q_2 - 4T_1) \frac{1}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) e^{\theta_2} = 0.$$

as  $\theta_2 = \frac{q_2}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ , according to (6). We have then:

$$(1 + e^{-\theta_2}) - \frac{\theta_2}{q_2} (q_2 - 4T_1) = 0,$$

or  $\theta_2 - e^{-\theta_2} = 1 + 4T_1 \frac{\theta_2}{q_2},$

or ( $R = 2$ )  $\theta_2 - e^{-\theta_2} = 2 \frac{T_1}{T_2} - 1 . . . . . (8a)$

From this we may find  $\theta_2$  by approximation, so also  $q_2$ , and  $q_1$  is found from (8). As  $q_2 - 4T_1 = \frac{q_2}{\theta_2} (1 + e^{-\theta_2})$ , we have:

$$q_1 = 4T_1 + 2 \frac{q_2}{\theta_2} e^{-\theta_2} = 4T_1 + 2 \frac{q_2}{\theta_2} \left(\theta_2 - 1 - 4T_1 \frac{\theta_2}{q_2}\right),$$

hence  $q_1 = 2q_2 - 4T_1 - 2 \frac{q_2}{\theta_2},$

or  $q_1 = 2q_2 - 4 \frac{T_1^2}{T_1 - T_2} . . . . . (8b)$

Now fig.3 holds for  $T_1 = 1/2 T_2$ , so (8a) becomes:

$$\theta_2 - e^{-\theta_2} = 3,$$

yielding  $\theta_2 = 3.05$ . Consequently  $q_2 = 2 \theta_2 T_1 = \underline{6.10 T_1}$ . Further according to (8b)  $q_1 = 2q_2 - 8T_1 = \underline{4.20 T_1}$ .

Of the curve I (comp. 8) I have determined the following points with  $T_1 = 1/2 T_2$ , so that  $\theta_2 = \frac{q_2}{2T_1}$ .

$q_2 = 1 T_1$	$e^{\theta_2} = 1,65$	$q_1 = 1,73 T_1$	$q_2 = 7 T_1$	$e^{\theta_2} = 33,1$	$q_1 = 4,175 T_1$
2 ..	2,72	2,92 ..	8 ..	54,6	4,14 ..
3 ..	4,48	3,63 ..	10 ..	148	4,08 ..
5 ..	12,2	4,15 ..	15 ..	1810	4,01 ..
6 ..	20,1	4,19 ..	20 ..	22000	4,00 ..

Really the maximum lies just past  $q_2 = 6T_1$ . (We saw already above, that for  $q_2 = 4T_1$  also  $q_1 = 4T_1$ ).

b. The curve II, viz.

$$q_2 = 4T_2 + \frac{2(q_1 - 4T_2)}{1 + e^{-q_1}} \dots \dots \dots (8II)$$

This curve separates the curves  $T = f(x)$  with *concave end* (left of this curve, because  $q_2$  is then smaller than the second member) from that with a *convex end* (right of the curve, where  $q_2$  is larger).

For  $q_1 = 0$  also  $q_2 = 0$ , as  $\theta_1 = 0$ ; (*initial direction* again  $q_1 = q_2 (45^\circ)$ ); for  $q_1 = 4T_2$  also  $q_2 = 4T_2$ , and for  $q_1 = \infty$ ,  $q_2$  will approach to  $\frac{2q_1 - 4T_2}{1}$ , because  $e^{-q_1}$  approaches to 0. The *limiting direction* of the curve II is therefore given by  $q_2 = 2q_1$ , or  $q_1 = \frac{1}{2} q_2$ . ( $26^\circ, 5$ ).

It will necessarily cut I. When  $T_2 = \frac{1}{2} T_1$ , this point of intersection  $S_1$  lies somewhat on the left of the maximum  $M_1$ . It is found by combining

$$q_1 = 4T_1 + \frac{2(q_2 - 4T_1)}{1 + e^{q_2/2T_1}} \quad \text{and} \quad q_2 = 2T_1 + \frac{2(q_1 - 2T_1)}{1 + e^{-q_1/2T_1}}$$

By approximation we find  $q_2 = 5,90T_1$ ,  $q_1 = 4,19T_1$ .

The further calculation leads to the following summary.

$q_1 = 1 T_1$	$e^{-\theta_1} = 0,61$	$q_2 = 0,76 T_1$	$q_1 = 8 T_1$	$e^{-\theta_1} = 0,02$	$q_2 = 13,8 T_1$
3 ..	0,22	3,64 ..	10 ..	0,01	17,9 ..
4 ..	0,135	5,52 ..	15 ..	0,00	28,0 ..
5 ..	0,08	7,56 ..	20 ..	0,00	38,0 ..
6 ..	0,05	9,62 ..			

For  $q_1 = 2T_1 (= 4T_2)$  also  $q_2 = 2T_1$  (see above).

c. The curve III, i.e.

$$q_1 = -4T_1 + \frac{2(q_2 + 4T_1)}{1 + e^{-q_2}} \dots \dots \dots (8III)$$

For values of  $q_1$  larger than the second member the *beginning* of  $T=f(x')$  is *concave*; these curves lie therefore *above* the curve. In the same way all the lines  $T=f(x')$  with *convex* beginning lie below this curve.

Again  $q_1=0$ , when  $q_2=0$  (*initial direction*  $q_1=q_2(45^\circ)$ ). When  $q_2$  approaches to  $\infty$ ,  $q_1$  approaches to  $\frac{2q_2 + 4T_1}{1}$ , so the *limiting direction* becomes  $q_1=2q_2(63^\circ,5)$ . This curve lies entirely *outside* the two first, more to the left.

Some points of the curve III follow.

$q_2 = 1 T_1$	$e^{-q_2} = 0,61$	$q_1 = 2,20 T_1$	$q_2 = 8 T_1$	$e^{-q_2} = 0,02$	$q_1 = 19,6 T_1$
2 ..	0,37	4,78 ..	10 ..	0,01	23,8 ..
4 ..	0,13 <sup>5</sup>	10,1 ..	15 ..	0,00	34,0 ..
6 ..	0,05	15,0 ..	20 ..	0,00	44,0 ..

d. *The curve IV*, i. e.

$$q_2 = -4T_2 + \frac{2(q_1 + 4T_2)}{1 + e^{q_1}} \dots \dots \dots (8IV)$$

If  $q_2$  is smaller than the second member, the *end* of  $T=f(x')$  will be *concave*; these lines lie accordingly *left* of the curve; on the *right* the lines  $T=f(x')$  with *convex* end are found.

For  $q_1=0$  again  $q_2=0$  (*initial direction*  $q_1=q_2(45^\circ)$ ). If  $q_1=\infty$ ,  $q_2$  evidently approaches *asymptotically* to  $q_2=-4T_2$ , just as the curve I approached asymptotically to  $q_1=4T_1$ , when  $q_2=\infty$ . The curve IV lies therefore only for a small part within the region of the positive  $q_2$ , and will therefore necessarily cut the  $q_1$ -axis somewhere in  $S_2$ , and yield a *maximum* value  $M_2$  for  $q_2$  before that time. This curve too lies therefore entirely *outside* the preceding curves, and again more to the left.

The  $q_1$ -axis is cut, when  $(T_2 = \frac{1}{2} T_1)$

$$\frac{q_1 + 2T_1}{1 + e^{q_1/2T_1}} = T_1,$$

or when

$$e^{q_1/2T_1} - 2 \frac{q_1}{2T_1} = 1.$$

This is satisfied by

$$\frac{q_1}{2T_1} = 1,25^5 \quad \text{or} \quad q_1 = \underline{2,51 T_1}.$$

$$2T_1 = 1.25' \quad \text{or} \quad q_1 = \underline{\underline{2.51T_1}}$$

The maximum is found in exactly the same way as in I, and is determined by

$$\theta_1 - e^{-\theta_1} = 2 \frac{T_2}{T_1} - 1. \quad \dots \dots \dots (8c)$$

to which belongs :

$$q_2 = 2q_1 - 4 \frac{T_2^2}{T_1 - T_2} \cdot \dots \dots \dots (8d)$$

If  $T_2 = 1/2 T_1$ , then (8c) yields :

$$\theta_1 - e^{-\theta_1} = 0,$$

from which  $\theta_1 = 0,567$ , or  $q_1 = \underline{1,13 T_1}$ . According to (8d) we have :

$$q_2 = 2q_1 - 2T_1 = \underline{0,26 T_1}.$$

Further we have the following values for  $q_2$  for increasing values of  $q_1$ .

$q_1 = 2 T_1   e^{q_1} = 2,72  $	$q_2 = 0,16 T_1  $	$q_1 = 10 T_1   e^{q_1} = 148  $	$q_2 = -1,84 T_1$
4 ,,   7,39	-0,57 ,,	15 ,,   1810	-1,98 ,,
6 ,,   20,1	-1,24 ,,		

Already at  $q_1 = 15 T_1$  the limiting direction  $q_2 = -4 T_2$  (here  $= -2 T_1$ ) has been all but reached.

IV. So we have seen, that the four limiting curves (see fig.3), which divide the  $q_1, q_2$ -space into different fields, radiate from the origin ( $q_1 = q_2 = 0$ ) in the space. All of them touch in the origin the straight line  $q_1 = q_2$ , the former two on the right, the latter two on the left. Only I is intersected by II; IV falls for the greater part outside the positive region; I and IV show maxima.

Below I and on the right of II lies the field A of the convex shaped meltingpoint-curves.

Between I and II on the left of the point of intersection  $S_1$  lies a small region  $B_1$ , where the *end* of  $T = f(x)$  has become concave; on its right is the region  $B_2$ , where the *beginning* of  $T = f(x)$  has become concave.

Between II and III (on the left of  $S_1$ , between I and III) lies the field C, where  $T = f(x)$  is concave throughout its course,  $T = f(x')$  convex.

Between III and the  $q_1$ -axis (below  $S_2$  between III and IV) lies the field D, where only the *end* of  $T = f(x')$  is still convex.

Finally there is still a very small region between IV and the  $q_1$ -axis, where the meltingpoint curve — both  $T = f(x)$  and  $T = f(x')$  — is concave throughout its course.

If we assume a fixed value for  $q_2$ , e.g.  $q_2 = 3 T_1$ , and vary  $q_1$  from

0 tot  $\infty$ , we pass successively through the four regions  $A$ ,  $B_1$ ,  $C$  and  $D$ . For  $q_2 = 10 T_1$  e.g. we should pass through the region  $B_2$  instead of through  $B_1$ .

If  $q_1$  is assumed to be constant, e.g.  $= 1 T_1$ , we pass successively through the fields  $A$ ,  $B_1$ ,  $C$ ,  $D$  and  $E$ , when  $q_2$  decreases from  $\infty$  tot 0.

Fig.4 gives a representation of the first mentioned transition, viz. for  $q_2 = 3 T_1$ .

Between the meltingpoint-curves, marked 2,4 and 2,8 (so holding for  $q_1 = 2,4$  and  $2,8 T_1$ ), the transition from  $A$  to  $B_1$  (hatched) is situated. Between 3,4 and 3,8 (see the hatched parts) is the transition from  $B_1$  to  $C$ . Between 7 and 8 (in this case for  $T = f(x')$ ) that from  $C$  to  $D$ . Further the cases  $q_1 = 1$ ,  $q_1 = 2$  ( $A$ ),  $q_1 = 5$  ( $C$ ) and

$$q_2 = 3 T_1$$

$q_1 =$	$1 T_1$	$2 T_1$	$2.4 T_1$	$2.8 T_1$	$3.4 T_1$	$3.8 T_1$	$5 T_1$	$7 T_1$	$8 T_1$	$10 T_1$
$T = 0.95 T_1$	$x' = 0.008$	0.016	0.019	0.022	0.026	0.029	0.038	0.051	0.057	0.069
	$x = 0.033$	0.066	0.074	0.081	0.11	0.12	0.16	0.21	0.24	0.28
0.90 "	$x' = 0.019$	0.036	0.043	0.052	0.058	0.066	0.080	0.10	0.11	0.13
	$x = 0.072$	0.14	0.16	0.185	0.22	0.25	0.30	0.39	0.43	0.50
0.85 "	$x' = 0.039$	0.072	0.072	0.082	0.096	0.10	0.13	0.16	0.17	0.19
	$x = 0.111$	0.21	0.25	0.28	0.33	0.36	0.44	0.55	0.59	0.67
0.80 "	$x' = 0.053$	0.093	0.11	0.12	0.14	0.15	0.18	0.22	0.23	0.256
	$x = 0.16$	0.29	0.34	0.38	0.44	0.47	0.56	0.67	0.72	0.785
0.75 "	$x' = 0.082$	0.14	0.16	0.18	0.20	0.215	0.25	0.29	0.30	0.32
	$x = 0.22$	0.39	0.44	0.48	0.55	0.58	0.67	0.78	0.815	0.87
0.70 "	$x' = 0.125$	0.20	0.23	0.25	0.28	0.29	0.33	0.36	0.38	0.39
	$x = 0.295$	0.48	0.54	0.59	0.65	0.69	0.77	0.86	0.89	0.928
0.65 "	$x' = 0.19$	0.29	0.32	0.35	0.37	0.39	0.43	0.46	0.47	0.48
	$x = 0.38$	0.59	0.65	0.69	0.75	0.78	0.85	0.918	0.928	0.934
0.60 "	$x' = 0.305$	0.43	0.46	0.48	0.51	0.525	0.555	0.58	0.59	0.60
	$x = 0.50$	0.71	0.76	0.80	0.84	0.87	0.915	0.960	0.971	0.986
0.55 "	$x' = 0.52$	0.64	0.665	0.695	0.71	0.72	0.735	0.75	0.755	0.76
	$x = 0.68$	0.84	0.87	0.913	0.927	0.910	0.965	0.980	0.991	0.997

$q_1 = 10(D)$  have been traced. The curves 2,8 and 3,4 represent therefore the type  $B_1$  with convex beginning and concave end for  $T = f'(v)$ . The calculations (according to formulae (4)) are summarized in the annexed table, i.e. for  $T_2 = \frac{1}{2} T_1$ , to which fig.3 applies.

With this change of  $q_1$  we do not enter the region  $E$ ; therefore  $q_2$  would have to be smaller than  $0,26 T_1$  (see above).

V. It remains to answer the question, to what modifications the fields and their limits drawn in fig. 3 are subjected, when  $T_2$  is not  $\frac{1}{2} T_1$ , but e.g.  $0,9 T_1$  or  $0,1 T_1$ .

The initial directions of the curves I to IV remain quite the same, also the final directions, but between them there are some modifications; specially the place of the points of intersection and of the maxima is changed.

a. If  $T_2$  is no longer  $0,5 T_1$ , but e.g.  $0,9 T_1$ , so that  $T_2$  and  $T_1$  are *very near* to each other, we find for the maximum  $M_1$  from (8a) and (8b):

$$\theta_2 - e^{-\theta_2} = 1^2/9 \quad ; \quad q_1 = 2q_2 - 40T_1,$$

yielding  $\theta_2 = 1,45^5$ , hence, as  $\theta_2 = \frac{q_2}{2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$  is now  $\frac{q_2}{18T_1}$ ,  $q_2 = 26,2 T_1$ . For  $q_1$  we find then  $q_1 = 12,4 T_1$ .

The maximum has now got quite outside the limits of the values of  $q$  which occur practically, so that the curve I now gradually rises within these limits. (fig.5).

The point of intersection of I with II has not been displaced much. We find now for it  $q_2 = 5,85 T_1$ ,  $q_1 = 5,55 T_1$ , so that the value of  $q_2$  has remained nearly constant.

The consequence of the modified course of the curves I and II is, that the region  $B_1$  has all but disappeared; on the left of  $S_1$  I and II nearly coincide; the region  $B_2$  has strongly diminished.

But also  $C$  and  $D$  have considerably diminished, so that the greater part of the space is left for  $A$  and  $E$ .

The considerable increase of the region  $E$  is due to the fact, that the point of intersection of the curve IV with the  $q_1$ -axis lies much higher than in fig. 3, and that the maximum has moved considerably to the right. In fact we find for the point of intersection mentioned:

$$\frac{q_1 + 3,6T_1}{1 + e^{q_1/18T_1}} = 1,8 T_1, \quad \text{or} \quad e^{q_1/18T_1} - 10 \frac{q_1}{18T_1} = 1.$$

from which  $\frac{q_1}{18T_1} = 3,577$ , so  $q_1 = \underline{\underline{64,4 T_1}}$ .

The maximum is given by (8c) and (8d), viz.

$$\theta_1 - e^{-\theta_1} = 0,8 \quad ; \quad q_2 = 2q_1 - 32,4 T_1,$$

giving  $\theta_1 = 1,125$ , so  $q_1 = \underline{20,3 T_1}$ ,  $q_2 = \underline{8,2 T_1}$ .

In the following table some more data are given, which have been used for the construction of fig.5.

<i>Curve I</i>	$q_2/T_1 = 1$	3	5	8	10	15	20	25	30	40	50	100	150	}
	$q_1/T_1 = 1,09$	3,09	4,86	7,13	8,37	10,7	11,9	12,3 <sup>s</sup>	12,2 <sup>6</sup>	11,0	9,39	4,74	4,07	
<i>Curve II</i>	$q_1/T_1 = 1$	2	4	6	8	10	15	20	30	40	60	100	}	
	$q_2/T_1 = 0,93$	1,91	4,04	6,40	8,96	11,7	19,5	28,3	48,0	69,3	112 <sup>s</sup>	196		
<i>Curve III</i>	$q_2/T_1 = 1$	2	4	6	8	10	15	20	30	40	60	100	}	
	$q_1/T_1 = 1,14$	2,33	4,88	7,65	10,6	13,8	22,5	32,1	53,2	75,4	120	203		
<i>Curve IV</i>	$q_1/T_1 = 1$	3	5	8	10	15	20	25	30	40	50	100	150	}
	$q_2/T_1 = 0,87$	2,45	3,81	5,46	6,32	7,67	8,09	7,82	7,08	4,93	2,68	-2,8	-3,53	

b. Let us now take  $T_2 = \underline{0,1 T_1}$ , so that the two temperatures of melting lie *very far* apart. This case (see fig.6) agrees more closely with that for which  $T_2 = 0,5 T_1$ ; only the maximum of the curve II has got nearer to  $q_2 = 4 T_1$ , and the point of intersection of II with I has moved much farther to the right. This has made the field  $B_1$  considerably larger than in the case  $T_2/T_1 = 0,5$ , which field had nearly vanished for  $T_2/T_1 = 0,9$ .

But nearly the whole of curve IV lies now outside the positive region, so that the appearance of bi-concave meltingpoint-curves is almost excluded.

The maximum of I is determined by

$$\theta_2 - e^{-\theta_2} = 19 \quad ; \quad q_1 = 2q_2 - 4^{1/2} T_1,$$

yielding  $\theta_2 = 19$ . As  $\theta_2 = \frac{q_2}{2^{1/2} T_1}$ , so  $q_2 = \underline{4^2/9 T_1}$ ,  $q_1$  being  $\underline{4,0 T_1}$ .

For the point of intersection of II with I we find, as  $e^{-\theta_2}$  is very large and  $e^{-\theta_1}$  very small,

$$q_1 = \underline{4,0 T_1}, \quad q_2 = 2q_1 - 4T_2 = 8,0 T_1 - 0,4 T_1 = \underline{7,6 T_1}.$$

The curve IV cuts the  $q_1$ -axis, when

$$0,2 T_1 = \frac{q_1 + 0,1 T_1}{1 + e^{\frac{q_1}{2^{1/2} T_1}}},$$

so when 
$$0,2 e^{\frac{q_1}{2^{1/2} T_1}} = \frac{q_1}{T_1} + 0,2,$$

or 
$$e^{\frac{q_1}{2T_1}} - \frac{10}{9} \cdot \frac{q_1}{2T_1} = 1$$

This gives  $\frac{q_1}{2T_1} = 0.203$ , hence  $q_1 = \underline{0.406 T_1}$ .

The maximum is found from

$$\theta_1 - e^{-\theta_1} = -0.8 ; q_2 = 2 q_1 - 0.044 T_1.$$

This is satisfied by  $\theta_1 = 0.1025$ , hence  $q_1 = \underline{0.0228 T_1}$ ,  $q_2 = \underline{0.0012 T_1}$ .

We can further calculate the following points of the four curves.

<i>Curve I</i>	$q_2/T_1 =$	$1/2$	$2/3$	$3/4$	$4/5$	$5/6$	$10/9$	$20/9$		
	$q_1/T_1 =$	1.06	1.97	3.15	3.68	3.89	3.95	4.00		
<i>Curve II</i>	$q_1/T_1 =$	$1/2$	$2/3$	$3/4$	$4/5$	$5/6$	$10/9$	$20/9$	3	4
	$q_2/T_1 =$	0.040	0.14	0.48	0.91	1.36	1.81	4.04	5.60	7.60
<i>Curve III</i>	$q_2/T_1 =$	$1/2$	$2/3$	$3/4$	$4/5$	$5/6$	$10/9$	$20/9$	3	
	$q_1/T_1 =$	1.12	2.17	3.83	4.89	5.60	6.15	8.44	10.0	
<i>Curve IV</i>	$q_1/T_1 =$	$1/2$	$2/3$	$3/4$	$4/5$	$5/6$	$10/9$	$20/9$		
	$q_2/T_1 =$	-0.014	-0.066	-0.20	-0.30	-0.35	-0.38	-0.40		

c. Hence when we draw near to the limiting case  $T_2 = T_1$ , all four curves will evidently approach to the straight line  $q_1 = q_2$ , which cuts the angle of the coordinates in two equal parts. Fig.5 is to a certain extent already a representation of this case.

If, however,  $T_2$  is very small, so that  $T_2/T_1$  approaches to 0, then I passes evidently into the straight line  $q_1 = 4T_1$ ; II into  $q_2 = 2q_1$ ; III into  $q_2 = 0$ , so into the  $q_1$ -axis; IV into  $q_2 = -4T_2 = 0$ , so again into the  $q_1$ -axis. Of this fig.6 gives already an idea.

As to the two maxima and the two points of intersection, we have finally the following summary.

	$M_1$					$M_2$				
$T_2/T_1 = 0$	0,1	0,5	0,9	1		0	0,1	0,5	0,9	1
$q_2/T_1 = 4$	4,2	6,1	26,2	$\infty$		0	0,0012	0,26	8,2	$\infty$
$q_1/T_1 = 4$	4,0	4,2	12,4	$\infty$		0	0,0228	1,13	20,3	$\infty$
	$S_1$					$S_2$				
$T_2/T_1 = 0$	0,1	0,5	0,9	1		0	0,1	0,5	0,9	1
$q_2/T_1 = 8$	7,6	5,9	5,85	4		0	0	0	0	0
$q_1/T_1 = 4$	4,0	4,2	5,55	4		0	0,045	2,51	64,4	$\infty$

And in this way I think that the ideal case  $a = 0$ ,  $a' = 0$  has been sufficiently elucidated.

**Physics.** — *“Isothermals of mixtures of oxygen and carbon dioxide.*

*I. The calibration of manometer and piezometer tubes”.* By W. H. KEESOM. Communication N° 88 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of September 26, 1903).

§ 1. With a view to the investigations of isothermals, critical and condensation phenomena, of which I hope to give the results in a following paper, I have carefully calibrated a manometer and a piezometer tube. The results of these calibrations have been reduced according to a method to which Prof. KAMERLINGH ONNES has drawn my attention. According to that method the bore of the tube is represented by some terms of a series of FOURIER, the coefficients of which are derived from the observations. Thus we start from a continuous representation of that bore in opposition to the discontinuous variations which we must adopt when we derive mean bores from the length of the mercury column at different places, and regard them as bores at the middle of the column. From the following may be judged what can be reached by means of this method.<sup>1)</sup>

§ 2. The manometertube was constructed after the model described in Comm. N° 50 of the Phys. Lab. at Leiden,<sup>2)</sup> differing herein that with a view to the higher pressures a ring was blown on to the part  $b_3$ <sup>3)</sup>, thus preventing the tube from moving along the cement in consequence of which the thinwalled part  $a_3$  would be pressed against the steel of the flanged tube, while the tube  $h_3$  is bent parallel to the length of the tube with the same purpose and in the manner as has been described in Comm. N° 69 (These Proc. III March 30, 1901, p. 625). The stem ( $c_3$  of fig. 4 Comm. N° 50), graduated in mm., had a length of 50 cm., the innerbore was 0.83 mm., the outer bore 6 mm., the capacity of the reservoir  $a_3$  was about 25 cc., the widened part  $d_3$  above had an inner bore of 2.6 mm., an outer bore of 9 mm. and had been taken so long that the manometer, filled with hydrogen, could indicate pressures from about 60 to about 190 atmospheres. The upper cylindrical part of the experimental tube for the investigation of the

<sup>1)</sup> In consideration of the circumstance that with these tubes observations have been made which will form the subject of following papers, we shall give already here for the sake of simplicity some data on stem calibration, together with some remarks on the way in which the further data about these tubes are obtained.

<sup>2)</sup> These Proc. II June 24, 1899, p. 29.

<sup>3)</sup> See plate I, fig. 4 of that Comm.

mixture was originally long 50 cm. and divided in mm.'s, had an inner bore of about 2.6 mm., an outer bore of about 7 mm.

The relation of the bores of the graduated parts of the manometer tube and the experimental tube at different places was determined by repeatedly moving a mercury column of about 10 cm. length over 5 cm. and then measuring its length. To effect this the manometer tube was placed in a horizontal position and the places of the ends of the mercury column were read with an eye-glass. We avoided parallax by taking care that the nearest graduation on the glass should be seen to cover its image on the mercury. For the wider experimental tube this method could not be used owing to the change of form of the mercury meniscus at the ends of the column in consequence of gravitation. Therefore the experimental tube was provided with a glass cock to which a narrow glass capillary had been connected. From this the air escaped only slowly under the excess of pressure of 10 cm. mercury. Then the tube was placed vertically after a mercury column of the length mentioned had been admitted. The latter could each time easily be moved over 5 cm. and the position of the ends read.

Then a longer mercury column was admitted into the tube in order to derive the mean bore from its weight. The bore of the above mentioned tube under the great reservoir ( $f'_s$ ), and also the volume of the reservoir were then determined by weighing the mercury.

§ 3. As an instance of the process of the calibrations and the

T A B L E I.

$M$	$L$	$\Delta$
6.90	11.40	+0.11
9.96 <sup>s</sup>	11.33	+0.04
14.98 <sup>s</sup>	11.31	+0.02
19.89	11.30	+0.01
24.76	11.30	+0.01
30.08 <sup>s</sup>	11.31	+0.02
35.02 <sup>s</sup>	11.25	-0.04
39.90	11.20	-0.09
44.22	11.18	-0.11
mean: 11.29		

calculations the data about the manometer will be given. The graduated tube has been calibrated twice, in 1901 (*A*) and in 1902 (*B*). I shall give here the data and the calculations concerning calibration *B*. Calibration *A* has been made in entirely the same way: the results of it will be given at the end of this paper and compared with those of *B*. Table I shows the results of the calibrations with the mercury column; column *M* contains the means, *L* the length of the mercury thread,  $\Delta$  the difference from the mean length. The temperature could be considered as having remained constant.

## T A B L E II.

Ends of the mercury column:			
1st position:	3.79 <sup>3</sup>	49.98 <sup>5</sup>	temp. 20.7
2d    "        "	30.35	in the graduated stem,...	9.25 mm. above
			the division of the
			thin capillary $e_3$ :
3d    "        "	2.80	49.00	» 20.65
			» 20.6
Weight of the mercury (in vacuo): 3.3777 gr.			

Calculation :

Let  $s$  be the bore of the tube at an arbitrary place, indicated by the coordinate  $x$  (from 0 to 50). We may put :

$$s = s_n + d$$

where  $s_n$  is a particular, normal, bore.

The volume between the 2 divisions  $p$  and  $q$  will be :

$$V_p^q = \int_p^q s \, dx = \int_p^q (s_n + d) \, dx = s_n(q - p) + \int_p^q d \, dx \quad . \quad (1)$$

The length of the mercury column :

$$q - p = m + \Delta$$

if  $m$  = the mean length (comp. table I). If  $V_k$  represents the volume of the mercury column then :

$$V_k = s_n m + s_n \Delta + \int_p^q d \, dx.$$

We may choose  $s_n$  so that :

$$m s_n = V_k,$$

then :

$$\Delta = -\frac{1}{s_n} \int_p^q d \, dx = -\int_p^q d' \, dx$$

if  $d' = \frac{d}{s_n}$ . If we knew the form of the function  $d'$ , we might derive

a number of equations from table I to determine the coefficients occurring there. Although the form of that function is unknown, yet  $d'$  for  $x$  between 0 and  $l$  must be representable by a series of FOURIER. It may now be asked whether it is possible within the limits of the accuracy given by the observations, to represent  $d'$  by some terms of a series of FOURIER. Therefore I have put :

$$d' = a'_1 \cos \frac{\pi x}{l} + a'_2 \cos \frac{2\pi x}{l} + a'_3 \cos \frac{3\pi x}{l},$$

where  $l$  is the length of the tube:

The term  $a'_0$  is omitted, because, in connection with the circumstance that  $\Delta$  represents the difference between the length of the mercury column and the mean length, we could expect beforehand that it would become small.

For  $-\Delta = \int_p^q d' . dx$  we then find, if we bear in mind that  $q - p = m + \Delta$ , where  $\Delta$  may be put small:

$$\begin{aligned} -\Delta = a'_1 & \left\{ \frac{2l}{\pi} \sin \frac{\pi}{2l} m + \Delta \cos \frac{\pi}{2l} m \right\} \cos \frac{\pi}{l} \frac{q+p}{2} \\ & + a'_2 \left\{ \frac{l}{\pi} \sin \frac{\pi}{l} m + \Delta \cos \frac{\pi}{l} m \right\} \cos \frac{2\pi}{l} \frac{q+p}{2} \\ & + a'_3 \left\{ \frac{2l}{3\pi} \sin \frac{3\pi}{2l} m + \Delta \cos \frac{3\pi}{2l} m \right\} \cos \frac{3\pi}{l} \frac{q+p}{2}. \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \dots \quad (2)$$

For the case under consideration  $l = 50$ ,  $m = 11.29$ , so that if as in table I we put:  $\frac{q+p}{2} = M$ :

$$\begin{aligned} -\Delta = a'_1 & \left\{ 11.05 + 0.94 \Delta \right\} \cos \frac{\pi}{l} M \\ & + a'_2 \left\{ 10.37 + 0.76 \Delta \right\} \cos \frac{2\pi}{l} M \\ & + a'_3 \left\{ 9.28 + 0.48 \Delta \right\} \cos \frac{3\pi}{l} M. \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \dots \quad (3)$$

The data of table I now lead to the equations combined in table III: first I have derived from table I the values of  $L$  for  $M = 10$ , 15 etc., as this offers some advantage in the calculations (the value  $L$  with  $M = 6.90$  is kept, as it did not seem advisable to me to extrapolate as far as  $M = 5$ ).

TABLE III.

-- 0.11 =	10.13 $a'_1$ +	6.76 $a'_2$ +	2.49 $a'_3$
-- 0.04 =	8.97 $a'_1$ +	3.07 $a'_2$ -	2.74 $a'_3$
-- 0.02 =	6.51 $a'_1$ -	3.07 $a'_2$ -	8.83 $a'_3$
-- 0.01 =	3.26 $a'_1$ -	8.40 $a'_2$ -	7.51 $a'_3$
-- 0.01 =	0.00 $a'_1$ -	10.38 $a'_2$ +	0.00 $a'_3$
-- 0.02 =	- 3.19 $a'_1$ -	8.41 $a'_2$ +	7.52 $a'_3$
+ 0.04 =	- 6.47 $a'_1$ -	3.05 $a'_2$ +	8.81 $a'_3$
+ 0.09 =	- 8.88 $a'_1$ +	3.04 $a'_2$ +	2.73 $a'_3$
+ 0.11 <sup>s</sup> =	- 10.42 $a'_1$ +	8.33 $a'_2$ -	5.42 $a'_3$

TABLE IIIb.

+ 5.14 $b'_5$
+ 0.00 $b'_5$
- 6.24 $b'_5$
+ 0.00 $b'_5$
+ 6.24 $b'_5$
+ 0.00 $b'_5$
- 6.25 $b'_5$
+ 0.00 $b'_5$
+ 6.26 $b'_5$

By means of the method of least squares<sup>1)</sup>, we find the normal equations combined in table IV.

TABLE IV.

475.8 $a'_1$ -	17.92 $a'_2$ -	130.65 $a'_3$ +	3.8284 = 0
- 17.92 $a'_1$ +	401.4 $a'_2$ -	28.31 $a'_3$ -	0.6606 = 0
- 130.65 $a'_1$ -	28.31 $a'_2$ +	319.0 $a'_3$ +	0.0882 = 0
- 13.31 $a'_1$ -	60.33 $a'_2$ -	21.02 $a'_3$ +	182.6 $b'_5$ + 0.0331 = 0

TABLE IVb.

- 13.31 $b'_5$
- 60.33 $b'_5$
- 21.02 $b'_5$

These equations yield :

$$\left. \begin{aligned} a'_1 &= -0.00908, \\ a'_2 &= 0.000964, \\ a'_3 &= -0.00391. \end{aligned} \right\} \dots \dots \dots (4)$$

By means of the equation (3) we can now calculate the values of  $\Delta$  for the different values of  $M$  in order to judge whether they agree sufficiently with the values given by the experiment. Then in the second number we may assign to  $\Delta$  the values of table I, and so use the coefficients given in table III, as these terms have little influence on the result. It now appeared that it was advantageous

<sup>1)</sup> Although each of the equations (3) contains 2 quantities deduced from observation, I have not applied here the method described in Supplement N<sup>o</sup> 4 to the Communications from the Phys. Lab. of Leiden, These Proc. V Sept. 27, 1902 p. 236 on the reduction of equations of observations containing more than one measured quantity, because  $M$  in comparison with  $\zeta$  may be supposed to be accurately known.

to add a fourth term to the equation (3), viz. one that contained the factor  $\sin \frac{5\pi}{l} M$ . Independent of this, I had arrived at the same conclusion in the calculation of the calibration  $A$ . Therefore I put :

$$d = a'_1 \cos \frac{\pi x}{l} + a'_2 \cos \frac{2\pi x}{l} + a'_3 \cos \frac{3\pi x}{l} + b'_5 \sin \frac{5\pi x}{l} \dots \quad (5)$$

so that we had to add to the second member of (2) :

$$+ b'_5 \left\{ \frac{2l}{5\pi} \sin \frac{5\pi}{2l} m + \Delta \cos \frac{5\pi}{2l} m \right\} \sin \frac{5\pi}{l} \frac{p+q}{2} \dots \quad (2b)$$

and to the second member of (3) :

$$+ b'_5 \left\{ 6.24 - 0.20 \Delta \right\} \sin \frac{5\pi}{l} M \dots \dots \quad (3b)$$

To the equations of table III we had to add the terms combined in table III*b*, to those of table IV to the first members the terms given in table IV*b*, and also the fourth equation given there. These equations gave :

$$\begin{aligned} a'_1 &= -0.00915 \\ a'_2 &= 0.000796 \\ a'_3 &= -0.00402 \\ b'_5 &= -0.001048 \end{aligned} \left\{ \dots \dots \dots \quad (6)$$

By means of these we have derived from the equation (3) with the supplementary term (3*b*) the values for  $\Delta$  for the different values of  $M$ . The results are given in table V under the heading  $\Delta_c$ , while column  $\Delta_o$  shows the observed values, and the last column contains

T A B L E V.

$M$	$\Delta_c$	$\Delta_o$	$\Delta - \Delta_o$
6.90	+ 0.103	+ 0.11	- 0.007
10	+ 0.069	+ 0.04	+ 0.029
15	+ 0.020	+ 0.02	0.000
20	+ 0.006	+ 0.01	- 0.004
25	+ 0.015	+ 0.01	+ 0.005
30	+ 0.007	+ 0.02	- 0.013
35	- 0.028	- 0.04	+ 0.012
40	- 0.073	- 0.09	+ 0.017
45	- 0.117	- 0.115	- 0.002

the differences. From this we derive for the probable error: 0.009, which with regard to the accuracy is permissible, so that the equation (5) with the coefficients (6) well represents our observations.

From equation (1) follows for the volume between the divisions 0 and  $Q$ :

$$V_0^Q = s_n \left\{ Q + \int_0^Q d' \cdot dx \right\} = s_n Q',$$

where

$$Q' = Q + q \text{ and}$$

$$q = \int_0^Q d' \cdot dx = \frac{l}{\pi} \left[ a'_1 \sin \pi \frac{Q}{l} + \frac{a'_2}{2} \sin 2\pi \frac{Q}{l} + \frac{a'_3}{3} \sin 3\pi \frac{Q}{l} + \frac{2b'_5}{5} \sin^2 \frac{5\pi}{2} \frac{Q}{l} \right].$$

Table VI gives for the values for  $Q$  from 0 to 50 the values computed in this way for  $Q'$ , the reduced readings. By means of this table we may inter alia judge of the irregularity of the tube.

T A B L E VI.

$Q$	$Q'$	$Q$	$Q'$	$Q$	$Q'$
0	0.000	17	16.878	34	33.864
1	0.987 <sup>5</sup>	18	17.878	35	34.866
2	1.975	19	18.878	36	35.869
3	2.962	20	19.878	37	36.872 <sup>5</sup>
4	3.950	21	20.877	38	37.877
5	4.938	22	21.877	39	38.882
6	5.927	23	22.875 <sup>5</sup>	40	39.888
7	6.917	24	23.874	41	40.895
8	7.908	25	24.872	42	41.903
9	8.900	26	25.870 <sup>5</sup>	43	42.911
10	9.893	27	26.868	44	43.920 <sup>5</sup>
11	10.888	28	27.867	45	44.931
12	11.884	29	28.865	46	45.942
13	12.881	30	29.864	47	46.954
14	13.879	31	30.863	48	47.966
15	14.878	32	31.863	49	48.980
16	15.878	33	32.863	50	49.993

The data of table II enable us now to determine the normal bore  $s_n$ . By means of table VI we find for the reduced length of the mercury column at 20°.6 C. the values :

46.232 cm.

46.215 cm.

mean: 46.223<sup>5</sup> cm.

Hence at 20° C.:  $s_n = 0.0053948 \text{ cm}^2$ .

From the data of table II we may also derive the volume of the widened part  $d_3$  (fig. 4 of Comm. N° 50). The bore of the capillary  $e_3$  was measured with a microscope by comparison with a fine graduation on glass by means of a micrometer eyepiece. The bore is : 0.000301 cm<sup>2</sup>. We then find for the volume of the part  $d_3$  between the division 50 on the graduated stem and the mark on the capillary at 20° C. : 0.14239 cc.

Using the value found for  $s_n$ , we may derive from table VI the volumes  $V_0^Q$  between the division 0 and the division Q, and then, using the volume found for the widened upper part, the volumes from division Q to the mark on the narrow capillary.

The calibration A has been made and reduced in entirely the same way. The results of either are combined in a table which indicates the volume for each centimeter division Q from 0 to 50. Table VII is an extract from that table.

T A B L E VII.

Q	$V_A$	$V_B$	% diff.
0	0.41161	0.41209	0.11
5	0.38487	0.38545	0.15
10	0.35800	0.35872	0.20
15	0.33125	0.33183	0.17
20	0.30441	0.30485	0.14
25	0.27731	0.27791	0.22
30	0.25028	0.25098	0.28
35	0.22357	0.22400	0.19
40	0.19673	0.19690 <sup>5</sup>	0.09
45	0.16938	0.16970	0.19
50	0.14189	0.14239	0.35

Column  $V_A$  contains the volumes from the mark on the narrow capillary to the division  $Q$  at  $20^\circ\text{C}$ ., as resulting from the calibration  $A$ ,  $V_B$  as resulting from the calibration  $B$ . The last column shows the percentage differences. The mean percentage difference between  $V_A$  and  $V_B$  in the complete table amounts to  $0.19\%$ , for the part from 0 to 41 inclusive, which only was used in the following observations:  $0.17\%$ . For our purpose this agreement is sufficient. From the fact that  $V_B - V_A$  is always positive it follows that the accuracy might be improved by more determinations of  $s_n$  and of the volume in the widened upper part. I hope to revert again to this subject in a following paper.

§ 4. To determine the capacity of the reservoir  $a_3$  with  $b_3$  (see fig. 4 l.c.) and also the bore of the part  $f'_3$ , the manometertube, which at the end  $e_3$  was provided with a cock with a fine point, was exhausted by the mercury vacuum pump and then filled with mercury in a reversed position until the mercury stood above at  $f'_3$  (in the drawing below). A quantity of mercury was drawn off twice and weighed so that we could determine the bore of  $f'_3$  at different places. The level of the mercury in the tube was read by means of a cathetometer. Then so much mercury was drawn off that the mercury still stood in the graduated stem  $e_3$ , and this was weighed. This served to determine the capacity of  $a_3 + b_3$ . The following results were obtained: the portion  $f'_3$  is divided into millimeters, the centimeterdivisions are marked from 0 to 6, 0 being nearest to  $a_3$ . It appeared that the bore could not be put constant; I have put:

$$s = s_0 \left\{ 1 + ax \right\},$$

and found:

$$a = 0.0058 \quad , \quad s_0 = 0.3564 \text{ (cm}^2\text{)},$$

so that

$$V_0 Q = 0.3564 \left\{ 1 + 0.0029 Q \right\} Q.$$

Table VIII (p. 541) contains the volumes from the division 0 to the division  $Q$  at  $20^\circ\text{C}$ .

For the calculation of the volumes of the menisci I have used SCHALKWIJK'S table occurring in Comm. N<sup>o</sup>. 67<sup>1)</sup>. For the volume between the division 0 on  $f'_3$  and the division 0 on  $e_3$  I found at  $20^\circ\text{C}$ . : 25.021 cc.

In the calibration of an experimental tube it will in general be

<sup>1)</sup> These Proc. III Jan. 27, 1901, p. 488.

T A B L E VIII.

$Q$	$V, \varrho$
1	0.3574
2	0.7169
3	1.0785
4	1.4421
5	1.8078
6	2.1756

necessary to take into account an electromagnetic stirrer, consisting of a soft iron rod in glass. In my case it consisted of a cylindrical portion with two bulbs at either end. The bores were measured with a micrometer screw, the length with a pair of sliding compasses. Each time when the experimental tube had to be refilled with a new quantity of gas, it had to be opened at the top in order to be cleaned. Because the stirrer had to be brought in, it was not possible to seal on a thin capillary as had been done for the manometer tube. Nor could the stirrer be placed into it beforehand, as this would be a hindrance in the cleaning and especially in the calibration with mercury. The volume of the top portion was determined each time after the measurements by cutting off so much from the top that on that piece one division at least was well visible (the upper divisions over a length of about 5 mm. were lost in the sealing). The fracture was ground flat, the piece after being cleaned and dried was entirely filled with mercury and the superfluous mercury was removed by sliding a properly cleaned flat piece of glass over the ground off end. The mercury was weighed, the position of the ground end was observed with regard to the divisions of the tube with a cathetometer and from this the volume of the top portion was derived.

**Physics.** — *“Isothermals of mixtures of oxygen and carbon dioxide. II. The preparation of the mixtures and the compressibility at small densities.”* By W. H. KEESOM. Communication N<sup>o</sup>. 88, continued, from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of September 26, 1903).

§ 1. In this paper I shall describe the preparation of the mixtures of accurately known composition in the mixing apparatus

described by KAMERLINGH ONNES and HYNDMAN, the determination of the compressibility of carbon dioxide and some mixtures of carbon dioxide and oxygen at ordinary pressures, together with the results.

§ 2. *The substances.* To obtain the carbon dioxide I used the method followed in the Physical Laboratory at Leiden<sup>1)</sup>, which together with the improvements made in the last years will be described in a paper on the apparatus and methods used in the Cryogenic Laboratory.

The purity of the carbon dioxide thus obtained appears from the increase of the pressure at the condensation at 25°.5 C. which amounts to only 0.07 atm.

The oxygen was prepared from potassium permanganate in the way described in Comm. N°. 78, These Proc. IV, April 1902, p. 768.

§ 3. *The preparation of the mixtures, the determination of the composition and the compressibility of the mixtures at ordinary pressures.* For the preparation of the mixtures I had at my disposal the apparatus described in Comm. N°. 84, These Proc. V, March 1903, § 21. As the operations required for the preparation of a mixture of accurately known composition are described there, I need not enlarge here on the details of this subject. I shall only mention that the apparatus was connected by means of the cock  $v_2$  (see plate II of that paper) to the apparatus for the preparation of oxygen, by means of cock  $v_3$  to the carbon dioxide reservoir, before which there was a drying tube filled with phosphorous pentoxide, and also to the experimental tube that had to be filled. After the mixture had been prepared, I have investigated in the volumenometer *B* the deviation from the law of BOYLE, in order to be able to express the volumes of my mixture at high pressures in terms of the theoretical normal volume. Although for my investigation an accuracy of  $\frac{1}{1000}$  would have been sufficient, I have gone a little further because in itself the knowledge of the deviations from the law of BOYLE at ordinary pressures is important and the apparatus without difficulty admits of a higher degree of accuracy. Taking all possible precautions an accuracy of  $\frac{1}{10000}$  might be reached. Yet I was satisfied with an accuracy of  $\frac{1}{5000}$ . To judge of this the following may serve:

1) Comp. among others KUNEN, Arch. Néerl. t. XXVI, p. 3 and VERSCHAFFELT Zittingsversl. Juni '95, Comm. N°. 18, Leiden.

## Measurement of the volume :

In order to judge of the accuracy we shall proceed as if we had to consider a quantity of gas measured in the first large bulb  $Eb_1$ , above (see l. c. plate II fig. 1). There the relative error is largest as the small bulb  $Eb_2$  above is only used for auxiliary measurements. The cathetometer used certainly reads well at 0.04 mm. : let the error be 0.02 mm. With a bore of  $Eb_1$  of about 200 mm<sup>2</sup>, this gives an error of 4 mm<sup>3</sup> : on 250 cc. :  $\frac{1}{60000}$ .

The height of the mercury meniscus read in the volumenometer was on an average 0.140 cm. I have supposed that the volume of the mercury meniscus is found by multiplying the bore by  $\frac{3}{4}$  of the height. The mean height undoubtedly lies between the half and the whole height (cf. SCHALKWIJK Comm. N<sup>o</sup>. 67, These Proc. III Jan. 1901 p. 488), so that the error is certainly smaller than  $\frac{1}{4}$  of the height, say  $\frac{1}{8}$ . Hence this gives  $\frac{1}{8} \times 1.40$  mm. = 0.18 mm., on the volume an error of 36 mm<sup>3</sup> or  $\frac{1}{7000}$ . In order to reach an accuracy of  $\frac{1}{10000}$  a more detailed investigation of the volumes of the mercury menisci at this radius (7.8 mm.) would be required, in the way as SCHALKWIJK l.c. has done for radii from 0.5 to 4 mm.

The variation of the volume due to temperature can accurately be accounted for.

Variation of volume owing to difference of pressure in and outside the volumenometer:

If we avail ourselves of the circumstance that the thickness of the wall is small as compared with the radius, a calculation applied to each bulb individually gives:

$$\frac{\delta V}{V} = \frac{3}{2} \frac{1-\mu}{E} \frac{(p_i - p_e) R}{d}$$

or for our case, putting:  $E = 6500$  K.G./mm.<sup>2</sup>,  $\mu = \frac{1}{4}$ , with  $R = 39$  mm.,  $d = 0.5$  mm.:

$$\frac{\delta V}{V} = 0.00000177 (p_i - p_e)$$

if  $p_i$  and  $p_e$  are expressed in centimeters of mercury; so that for  $p_i - p_e = 56$  cm.:  $\frac{\delta V}{V} = \frac{1}{10000}$ . For this a correction is applied

hence the error of the correction owing to the coefficient not being precisely known, may be neglected.

The volume in  $Eb$  above  $Eb_{s_2}$ , which could not be determined by means of mercury, may be determined with sufficient accuracy volumetrically, as we have to do with proportions of much larger volumes.

Measurement of the pressure:

In most cases it will be possible to follow the rule of making the adjustment of the mercury in the volumenometer at a mark so that the pressure of the gas above it is not less than 0.5 atm. For a measurement of the pressure 4 cathetometer readings are required; let us put for the probable error of the result:  $2 \times 0.02 = 0.04$  mm.;

this is on 40 cm.:  $\frac{1}{10000}$ . Only at the volumetric determination of the relation of  $Eb_2$  and what is above it to  $Eb_1$  the pressure was smaller, but this relation, being, as it has been said, only used as an auxiliary quantity, need not be so accurately known. The same may be said of the measurement of the remainder of the first gas in  $E$ , after as much gas as possible has been transferred to the mixing vessel  $F$ .

Although  $E$  had been accurately vertically mounted, so that the mercury menisci of both  $Eb_{s_2}$  and  $Eb_3$  could be seen sharply without altering the focusing of the cathetometer telescope, it yet appeared that the windows  $Eh_n$  were not exactly vertical, but that they all deviated from this position in the same direction at an angle estimated at  $0.2^\circ$  by means of a level fastened at right angles to a flat piece of steel. Therefore as the windows are not placed perpendicularly to the line of vision of the cathetometer telescope, refraction occurs, which causes an apparent displacement of the mercury meniscus of

$d \cdot i \cdot \frac{n-1}{n}$  cm.,  $d$  being the distance from the meniscus to the window,

$i$  the angle of the normal on the window and the horizon,  $n$  the refractive index of water. In our case ( $d = 8.6$  cm.,  $n = 1.33$ ) this displacement amounts to : 0.0075 cm. This gives on  $\frac{1}{2}$  atmosphere an

error of  $\frac{1}{5000}$ . As we have to do with relations of quantities to each

of which a correction in the same sense would have to be applied, the error in the result is smaller. If a higher degree of accuracy is wanted, the angle formed by the windows and the vertical will have to be determined more accurately, so that the correction may be applied. For our purpose this was not necessary.

Correction for the temperature of the mercury :

If the pressure amounts to say 0.5 atm., measured as the difference of two mercury columns of 76 and 38 cm. respectively, the temperature of the long column must be known precisely to within 0.5, if an accuracy of  $\frac{1}{5000}$  is required. We must assume that this is possible if the mercury columns together with the thermometers are packed in wool. The difference between the indications of the thermometer at the lower end and at the upper end of the barometer *Bar.* did not as a rule amount to more than 0.5 C., hence we may accept that the uncertainty caused by this in the knowledge of the temperature did not exceed by much 0.25 C. For the difference of the temperature of the mercury in *M* and *E* a correction is applied.

The capillary depressions are largest in the volumenometer, and of the order of say 0.07 mm. The uncertainty here is surely much smaller than the errors resulting from the windows not being vertical.

Corrections for the difference in level between the meniscus in *Bar.* below, and in *M*, and also those for the reduction of the pressure immediately above the mercury in *E* to the mean pressure of the gas above it, may be applied with sufficient accuracy.

Measurement of the temperature :

During the time of one measurement (25 minutes) the temperature by means of a thermostat of SCHALKWIJK <sup>1)</sup> can certainly be kept constant at 0.03 C., while if the water at constant temperature flows rapidly enough through *E*, the temperatures at the lower and at the upper end did not differ more. The temperature was read on a thermometer *Th* connected with the stirrer *Er*, which therefore could be placed in different positions. The thermometer was graduated in 0.05, so that 0.01 could be easily read; it has been repeatedly compared with a standard thermometer tested at the Reichsanstalt. As therefore the error in the measurement of temperature does not amount to 0.03 C., the accuracy is certainly

$$0.03 \times \frac{1}{300} = \frac{1}{10000}.$$

A portion of the volume (in the tubes *Eb<sub>g1</sub>* and *Eb<sub>g2</sub>*, which have an inner bore of 1.2 mm.) is not enclosed in the jacket. This volume is a little less than 1 cc. For its temperature which is put equal to the temperature of *M* a correction is applied. If in a measurement in the first bulb *Eb<sub>1</sub>*, we assume that in the temperature of that portion there is an error of 5°, the error in the mean

<sup>1)</sup> Comp. Comm. N<sup>o</sup>. 70, These Proc. IV May 25, 1901, p. 29.



temperature of the whole becomes 0.02 and may be disregarded, especially in consideration of the fact that the difference in temperature between the jacket and the surrounding atmosphere as a rule is less than 5° and therefore the error made will certainly be smaller.

Hence only in very unfavourable cases the error in the result will be larger than  $\frac{1}{5000}$ , and we may expect that in most cases the error will not exceed this amount.

To judge of the course of a measurement I have given in table IX (p. 546) the experimental figures of an adjustment for the determination of the deviation from the law of BOYLE of the mixture of 0.2 oxygen with 0.8 carbon dioxide. Column *A* contains the readings of the level (see Comm. N<sup>o</sup>. 60 These Proc. III Sept. 29, 1900 p. 312), *B* the readings of the cathetometer.

The volumenometer had beforehand been calibrated with mercury by Dr. C. ZAKRZEWSKI. Hence we knew at the same temperature the volumes of the bulbs  $Eb_1$ , measured between the middle marks on the glass screens  $E'f$ , and also the bores  $Eb_3$ ,  $Eb_4$ ,  $Eb_6$ ,  $Eb_7$ ,  $Eb_8$ . In the apparatus used the mercury could not be read while it stood in  $Eb_5$ , because owing to a former manipulation in the blow-pipe the bore at that place was not perfectly cylindrical. There the sum of the volumes of the two neighbouring bulbs had been measured.

To test this and also to determine the volume of  $Eb_2$  with what lies above it I have determined volumetrically the relation of the different volumes with dry air free from carbon dioxide. To account for the deviation from the law of BOYLE I could make use of coefficients of KAMERLINGH ONNES'<sup>1)</sup> series:

$$pv_A = A_A + \frac{B_A}{r_A} + \frac{C_A}{r_A^2} + \frac{D_A}{r_A^4} + \frac{E_A}{r_A^6} + \frac{F_A}{r_A^8},$$

put kindly at my disposal, which accurately represent to within 0.2% the conduct of air as indicated by AMAGAT's experiments. The three first coefficients are for 20° C:

$$\begin{aligned} A_A &= 1.0738 \\ B_A &= -0.40495 \times 10^{-3} \\ C_A &= 3.0178 \times 10^{-6}. \end{aligned}$$

We find for the relation of the volumes  $V_1$  and  $V_2$  which are filled with the same quantity of gas at the same temperature to pressures  $p_1$  and  $p_2$  to the first approximation:

<sup>1)</sup> Comm. N<sup>o</sup>. 71. These Proc. III June 29, 1901, p. 125.

$$\frac{V_1}{V_2} = \frac{p_2}{p_1} \left\{ 1 + \frac{B_A}{A_A^2} (p_1 - p_2) \right\} \dots \dots \dots (1)$$

if  $p_1$  and  $p_2$  are expressed in atmospheres ( $0^\circ \text{C}$ ,  $45^\circ$  northern latitude). A second approximation where the coefficient  $C_A$  would occur is not necessary with a view to the accuracy required.

TABLE Xa.

	<i>A</i>	<i>B</i>	<i>C</i>
$\frac{V_1}{V_0}$		8.878	
$\frac{V_2}{V_1}$	1.8913	1.8910	- 0.016
$\frac{V_1}{V_2}$	1.9396	1.9400	+ 0.022
$\frac{V_5}{V_4}$	1.2422	1.2420	- 0.012

TABLE Xb.

	<i>E</i>
$El_{81}$	0.005085
$El_7$	0.000675
$El_6$	0.000314
$El_4$	0.000165
$El_3$	0.000135

Table X shows the results of the calibration. There we have called:  $V_n$  the volume above  $El_{81}$ ,  $V_1$  the one above  $El_7$ ,  $V_2$  the one above  $El_6$ , etc. Column *A* of table Xa gives the relations of the volumes according to the mercury calibration, *B* according to the volumetrical determination, *C* the percentage differences. Column *E* of table Xb gives the relation of the volume of 1 mm. of the indicated bore to the entire volume above it. It may be seen that the agreement between the two calibrations is sufficient. In following calculations the mercury calibration has been adopted as being the more accurate.

For the calculation of the composition we derive from the measurements in the volumenometerdata, as those for the mixture 0.2 (oxygen in carbon dioxide) are combined in table XI. *A* contains the data of the oxygen in the volumenometer, *B* refers to the oxygen which has remained in *E* after the transference of the greater part into *B*, *C* refers to the carbon dioxide.

T A B L E XI.

	<i>A</i>	<i>B</i>	<i>C</i>
Volume . . .	0.99979 $V_2$	0.98905 $V_0$	0.99994 $V_5$
Pressure . . .	40.396	0.380	66.961
Temperature	19.81	19.53	19.83

First of all we may derive from  $B$  the pressure which the remainder of the oxygen would have exerted in the volume  $0.99979 V_2$  and at a temperature of  $19^\circ.81$  C. In this calculation the law of BOYLE may be applied with sufficient accuracy. We then find:  $0.022$  cm. The pressure which the quantity of oxygen transferred to the mixture would exert in the volume  $0.99979 V_2$ , at  $19^\circ.81$  C. is then represented with sufficient accuracy by:

$$40.396 - 0.022 = 40.374 \text{ cm.}$$

The pressures of the oxygen and the carbon dioxide may be reduced to the same temperature  $19^\circ.82$  C., by deriving coefficients of pressure variation from the series gives in Comm. N<sup>o</sup>. 71, or by means of the value for oxygen  $0.003674$  found directly by JOLLY, and the value  $0.003711$  which follows from CHAPPEIS' data (Trav. et Mém. du Bureau International des Poids et Mesures. t. II p. 124) for the "real" coefficient of pressure variation of carbon dioxide at  $20^\circ$  C. and an initial pressure of 1 atmosphere<sup>1)</sup>.

We find for the oxygen:  $40.375$ , for the carbon dioxide:  $66.959$  cm. If  $p_1, V_1$  are the pressure and the volume of the first gas,  $p_2, V_2$  of the second, it may be easily found that the number of molecules of the first gas is proportional to:

$$1 + \frac{p_1 V_1}{A_1^2} \frac{B_{A_1}}{A_1}$$

that of the second to:

$$1 + \frac{p_2 V_2}{A_2^2} \frac{B_{A_2}}{A_2}$$

where, at least with regard to the denominators,  $p_1$  and  $p_2$  are expressed in atmospheres. We find from the data of Comm. N<sup>o</sup>. 71, These Proc. III June 29, 1901 p. 130 and 132:

for oxygen:

$$\begin{aligned} A_{A_{20}} &= 1.074237 \\ B_{A_{20}} &= -0.74273 \times 10^{-3}. \end{aligned}$$

<sup>1)</sup> We shall not consider here the variation of the coefficient of pressure-variation with the initial pressure: this variation would be for a difference of 50 cm. in the initial pressure according to CHAPPEIS, i.e.,  $0.000034$ , which with a reduction of the pressure for  $1^\circ$  difference of temperature would give an error of only  $\frac{1}{30000}$ . Keeping in view the fact that such large differences in the temperature do not occur, this may be neglected.

For carbon dioxide we may use the value derived directly from observation which will be given later :

$$\frac{B_{A_{20}}}{A_{A_{20}}^2} = -0.005675.$$

These values may also be taken with sufficient accuracy for the temperature used (19°.82 C.). The composition of the mixture considered is easily found to be: 0.19942 (oxygen in carbon dioxide).

§ 4. In the volumenometer I have determined the compressibility at ordinary pressures as indicated in Comm. N°. 84, These Proc. V March 28, 1903, p. 641, for the mixtures with molecular proportions of 0.1994 and 0.3072 (oxygen in carbon dioxide), and also that for the pure carbon dioxide. Although this has already been done by REGNAULT<sup>1)</sup>, AMAGAT<sup>2)</sup>, FUCHS<sup>3)</sup>, LEDUC<sup>4)</sup> and lately by CHAPPUIS<sup>5)</sup> it seemed to me important to make that determination with the same carbon dioxide and in the same apparatus as for the mixtures, so as to have the most favourable circumstances for the comparison of the conduct of the mixtures with that of pure carbon dioxide.

Table XII gives the values directly derived from the observations for volume, pressure and temperature belonging to each other. The columns *A*, *B* and *C* refer to different adjustments with the same quantity of gas.

T A B L E XII.

*a.* Carbon dioxide.

	<i>A</i>	<i>B</i>	<i>C</i>
Volume . . . . .	0.99969 $V_5$	0.99995 $V_4$	0.99958 $V_2$
Pressure . . . . .	47.261	58.662	413.327 cm.
Temperature	19.99	20.02	19.97

*b.* Mixture with molecular proportion :  $x = 0.1994$ .

	<i>A</i>	<i>B</i>
Volume . . . . .	1.00028 $V_1$	0.99934 $V_2$
Pressure . . . . .	97.708	51.848 cm.
Temperature	20.03	19.96

1) Mém. de l'Inst. de France. t. XXI, p. 329.

2) Ann. de Chim. et de phys. (4) t. 29, p. 246, 1873.

3) Wied. Ann. Bd. 35, p. 430, 1888.

4) Recherches sur les Gaz, p. 86.

5) Trav. et Mém. du Bureau Internat. des Poids et Mesures, t. XIII, 1903.

c. Mixture with molecular proportion :  $x = 0.3072$ .

	A	B	C
Volume . . . . .	0.99975 $V_3$	0.99983 $V_4$	0.99972 $V_2$
Pressure . . . . .	48.188	59.839	115.752 cm.
Temperature	20.10	20.14	20.14

As an instance for the calculation we shall consider the last mixture more in detail. First the pressures were reduced to the mean temperature 20°.13 C., by means of the "real" coefficient of pressure variation  $\frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_r$  at 20° : 0.0034. <sup>1)</sup> This gave for A, B, C, 48.193, 59.837 and 115.748 cm. respectively. If  $p_1$ ,  $V_1$  and  $p_2$ ,  $V_2$  respectively represent a corresponding pressure and volume, we have to the first approximation, which for our case is sufficient :

$$1 - \frac{p_2 V_2}{p_1 V_1} = \frac{B_A}{A_A^2} (p_1 - p_2), \quad . . . . . (2)$$

where  $p_1$  and  $p_2$  are expressed in atmospheres. From this we may derive  $\frac{B_A}{A_A^2}$ . In the case considered we found:

$$\begin{aligned} \text{from A with C: } \frac{B_A}{A_A^2} &= -0.003579^s \\ \text{,, B ,, C: } & \frac{-0.003407}{\text{mean: } -0.003493} \quad \text{at } 20.13 \text{ C.} \end{aligned}$$

In the same way for carbon dioxide at 20°.00 C. :

$$\begin{aligned} \text{from A with B: } \frac{B_A}{A_A^2} &= -0.005814 \\ \text{,, A ,, C: } & \frac{-0.005536}{\text{mean: } -0.005675}, \end{aligned}$$

and for the mixture 0.2 at 20°.00 C. :

$$\frac{B_A}{A_A^2} = -0.003847.$$

If the coefficient of pressure variation were known (mean coefficient between 0° and 20°) we could easily derive  $A_{A,0}$  for the different cases. For if for the mixture 0.3 at  $t = 20.13$  in the equation:

<sup>1)</sup> Comp. p. 553.

$$p_{v,A} = A_{v,A} + \frac{B_{v,A}}{r_{v,A}} \dots \dots \dots (3)$$

we put  $v_A = 1$ , we obtain:

$$1 + \alpha_p \cdot 20,13 = A_{v,A} + B_{v,A},$$

if  $\alpha_p$  is the corresponding coefficient of pressure variation.

From the two relations between  $A_A$  and  $B_{v,A}$ ,  $A_A$  may be derived and then  $A_{A_0}$  may be found from the relation<sup>1)</sup>:

$$A_A = A_{A_0} (1 + 0.0036625 t) \dots \dots \dots (4)$$

A difficulty arises from the uncertainty of  $\alpha_p$  for the mixtures: an error in  $\alpha_p$  passes over into  $A_{A_0}$  20 times magnified. This may be avoided in the following manner:

As normal temperature we shall temporarily adopt 20° C., and then we write KAMERLINGH ONNES' equation for the area of the pressures considered here:

$$p V = V_{N_{20}} \left\{ A_K + \frac{B_K V_{N_{20}}}{V} \right\} \dots \dots \dots (5)$$

$V$  is the volume really occupied by the gas,  $V_{N_{20}}$  the normal volume at 20° C., viz. the volume occupied by the quantity of gas considered at 20° C. and 1 atmosphere.

Now:

$$\begin{aligned} A_K &= A_{K_{20}} \left\{ 1 + \frac{0.0036625}{1 + 20 \times 0.0036625} (t-20) \right\} \\ &- A_{K_{20}} \left\{ 1 + 0.0034125 (t-20) \right\} \dots \dots \dots (6) \end{aligned}$$

A comparison with

$$p V = V_N \left\{ A_A + \frac{B_A V_N}{V} \right\}, \dots \dots \dots (7)$$

where  $V_N$  is the normal volume at 0° C., gives the relations:

$$\begin{aligned} A_A \cdot V_N &= A_K \cdot V_{N_{20}} \\ B_A \cdot V_N^2 &= B_K \cdot V_{N_{20}}^2 \dots \dots \dots (8) \end{aligned}$$

whence:

$$\frac{B_A}{A_A^2} = \frac{B_K}{A_K^2} \dots \dots \dots (9)$$

Hence it is given that for the mixture 0.3 at 20° 13 C.:

$$\frac{B_K}{A_K^2} = - 0.003493.$$

From (5) follows, putting  $t = 20^\circ 13$  and  $V = V_{N_{20}}$ :

<sup>1)</sup> Comp. Comm. N°. 71, These Proc. III June 29, 1901, p. 130.

$$1 + 0.13 \alpha_{pK} = A_K + B_K.$$

$\alpha_{pK}$  represents the coefficient of pressure-variation of the mixture (the mean coefficient between  $20^\circ$  and  $t$ ), if the original pressure (at  $20^\circ$  C.) is 1 atm. From these two relations  $A_K$  may be derived; it must be remarked that now an error in  $\alpha_{pK}$  passes over diminished into the result. By means of (6)  $A_{K_{20}}$  may be derived from  $A_K$ .

So I found for the mixture under consideration:

$$\text{for } 20.13 \text{ C.: } A_K = 1.003969, \quad B_K = -0.003521.$$

Further I accepted for  $\alpha_{pK}$ : 0.003445, found by linear interpolation according to  $x$  between the value 0.003454 for carbon dioxide derived from CHAPPUIS' data, and the value 0.003423 for oxygen derived from JOLLY'S data. It then follows that  $A_{K_{20}} = 1.003524$ .

The different values thus found are combined in Table XIII.

T A B L E XIII.

	$A_{K_{20}}$	$x$	Weight.
Carbon dioxide	1.00574	0	1
Mixture 0.2	1.00388	0.1994	$\frac{2}{3}$
» 0.3	1.00352	0.3072	1
Oxygen	1.00064	1	1

For oxygen  $A_{K_{20}}$  is derived from the data for  $A_{A_{20}}$  and  $B_{A_{20}}$  given on p. 549.

I have put:

$${}_x A_{K_{20}} = 1 + a_0 (1-x)^2 + 2 a_{01} x (1-x) + a_1 x^2,$$

and have calculated the coefficients by means of the method of least squares. There  $x$  as compared with  ${}_x A_{K_{20}} - 1$  may be considered as perfectly accurately known. I found:

$$a_0 = 0.00570$$

$$a_{01} = 0.00142$$

$$a_1 = 0.00065.$$

In table XIV (p. 554) the values  $C'$  derived from them are compared with the values derived directly from observation  $C$ .

In order to derive the coefficients  $A_{A_0}$  from the coefficients  $A_{K_{20}}$  an accurate knowledge of the coefficient of pressure-variation is required. In a following paper, however, will be described how the coefficients  $A_{K_{20}}$  may be used to derive from the volume of a gas

T A B L E XIV.

	$0$	$t$	$0-t$
Carbon dioxide	1.00574	1.00570	+ 0.00004
Mixture 0.2	1.00388	1.00413	— 25
"    0.3	1.00352	1.00340	+ 12
Oxygen	1.00064	1.00065	— 1

measured at about  $20^{\circ}$  C the theoretical normal volume of that quantity of gas (at  $0^{\circ}$  C).

**Physics.** — "*Isothermals of mixtures of oxygen and carbon dioxide. III. The determination of isothermals between 60 and 140 atmospheres, and between  $-15^{\circ}$  C and  $+60^{\circ}$  C.*" By W. H. KEESOM. Communication N<sup>o</sup>. 88 (3<sup>rd</sup> part) from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of October 31, 1903).

§ 1. During my measurements of the isothermals of mixtures of oxygen and carbon dioxide it appeared desirable to take several precautions and to make some modifications in the usual methods. They will be described here in connection with and in behalf of following papers on the results obtained.

§ 2. *The arrangement.* The manometertube and the experimental tube which beforehand had been cemented into a steel flanged tube (comp. Comm. N<sup>o</sup>. 70 V, These Proc. IV June 29, '01 p. 107) were placed into steel pressure cylinders. For the shapes of these see also Comm. N<sup>o</sup>. 43, These Proc. I June 25, 1898, p. 83, fig. 2. The arrangement as drawn there has been modified, viz. the two pressure cylinders into which the aforementioned tubes were placed were entirely filled with mercury. They communicated at their lower ends by means of a steel tube and of a steel T-piece with each other and with a third pressure cylinder. This was filled partly with mercury partly with glycerine. To obtain pressure, glycerine was forced into it by means of a SCHÄFFER-BUDENBERG pump. This arrangement offers the advantage that the tubes filled with gas do not come into contact with the glycerine, and the mercury which is forced into the tubes only slightly with the glycerine. In this way it was very easy to redetermine the normal volume after lifting out the experimental tube from the pressure cylinder, while the mercury menisci in the tubes

kept good during a very long time and no or very little soil was deposited in the tubes.

The pressure cylinders and the connecting tubes had been well cleaned beforehand with benzene, which was removed by heating while air was sucked through. The connections were tightened by leather washers soaked in paraffin. The packing which had to prevent leakage of mercury along the pivot of the high pressure cocks through which the mercury passed which was to be forced into the observation tubes, consisted of rings cut from selected Spanish corks. During the observations the two observation cylinders were disconnected from that where the pressure of the glycerine was transferred to the mercury in order to be independent of leakage that might occur in the pump or in the glycerine lead<sup>1)</sup>. A perfectly tight fit of this enclosed portion even at the highest pressures was secured.

§ 3. *The measurement of the volumes.* The determination of the normal volume was made in the same way as has been described in Comm. N°. 70 V. These Proc. IV June 29, 1901, p. 107 and in Comm. N°. 78, These Proc. VI April 19, 1902, p. 761, especially the same precautions for the constant temperature and pressure were taken.

The normal volume was determined at least twice before and twice after the measurements. It must be recorded, however, that this was not done with the first quantity of carbon dioxide of which the isothermals from 25°.55 C. to 37°.09 C. were investigated, because the experimental tube had broken, while in the case of the manometer we may profitably substitute a direct comparison with a standard manometer, to which comparison I shall refer later.

I found for the normal volume of the hydrogen manometer:

22 Sept. '02:	23.217 cc.
..	23.194 ..
..	23.192 ..
12 Nov. ..	23.220 ..

As the first 3 measurements are not made in the bath of constant temperature I have in the calculation of the mean assigned the weight 3 to the last determination and have adopted  $V_N = 23.210^3$  cc.

From the following the advantage of a hydrogen manometer may appear<sup>2)</sup>. Most of the determinations with the first mixture (0.1 oxygen in carbon dioxide) were made with an air manometer. During the experiments phenomena occurred which pointed to variations of

<sup>1)</sup> Small variations of pressure could then be applied by screwing slightly in or out the pivot of one of the fine high pressure cocks in the enclosed portion.

<sup>2)</sup> Comp. Comm. N°. 50, These Proc. II June 24, 1899, p. 29.

the normal volume of this manometer. The manometer was removed from the pressure cylinder and the normal volume redetermined, and it appeared that from 22.114 cc. (May 9 1901) it had fallen to 22.056 cc. (Aug. 23 '02). After this the manometer has been calibrated for the second time (calibration *B*)<sup>1)</sup> and filled with hydrogen; of each of the isothermals determined some points have been tested by means of the hydrogen manometer. Column *C* of table XV gives the mean relation of the pressure measured with the hydrogen manometer and that measured with the air manometer, where for the normal volume of the latter we have taken the mean between those before and after the experiments. Column *A* gives the date, *B* the temperature relating to the isothermal.

TABLE XV.

A.	B.	C.
20 June '02	47.60	1.0020
20 » »	20.29	1.0017
23 » »	21.99	1.0016 <sup>5</sup>
24 » »	22.68	1.0023
25 » »	23.29	1.0013
26 » »	25.20	1.0019
mean :		1.0018

From column *C* we cannot derive a regular course in this short period, so that for these isothermals I have multiplied all the pressures measured with the air manometer by the coefficient 1.0018. On June 5, 6 and Aug. 21 points of the border curve have been determined. These could only be brought to harmonize with those determined later with the hydrogen manometer by multiplying the pressures by coefficients which are combined in the following table together with that afore-mentioned. Hence this shows the course of the variation during that period.

If we compare these figures with the values for the normal volume before and after the measurements, it appears that almost the entire variation has taken place during this last period. From May '01 to

<sup>1)</sup> Comp. this Comm. I. p. 534.

TABLE XVI.

5/6 June '02	1.0021 <sup>5</sup>
20 '26 " "	1.0018
21 Aug. "	0.9997

June '02 the manometer was but seldom used, and the pressure during that time was low, while the pressure in the months June–Augustus '02 was often and during a long time from 60 to 125 atmospheres. Hence it seems that this variation is much greater at a high than at a low pressure.

A similar variation of an air manometer with the time, probably owing to the absorption of oxygen in the mercury, has also been noted by KUTEXEN and ROBSON (*Phil. Mag.* Jan. '02 p. 150).

In the mixtures of the molecular proportions 0.1 and 0.2 of oxygen the variations of the normal volume were less than  $\frac{1}{1000}$ . In those cases we have accepted for the normal volume the mean of the values before and after the measurements.

On the other hand, in a mixture with a molecular proportion of 0.3072, which for some weeks had uninterruptedly been exposed to high pressure, the normal volume of 72.878<sup>5</sup> cc. before the experiments (15 June '03) had fallen to 70.980 cc. after the experiments (13 Aug.). It being highly probable that the variation of the normal volume involves a considerable variation in composition, the results of the measurements with this mixture which with regard to the end condensation pressures and volumes extended to  $-14^{\circ}.7$  C., will not be given here.

This also shows how very important it is that we should be able to determine the normal volume after the measurements<sup>1)</sup>.

From the observation of the volume occupied by the gas at a temperature of about 20° C. and a pressure of about 1 atmosphere we derived the volume which the gas would occupy at 20° C. and 1 atm. (75.9467 cm. mercury at Leiden, comp. Comm. N<sup>o</sup>. 70, *These Proc.* IV June 29, 1901, p. 111). Use was made of the coefficient of pressure variation given in this Comm. II, p. 553, and the law of BOYLE was applied. By multiplication by the values of the coefficients  $A_{K_{20}}$  given in table XIV p. 554 under  $C'$ , we find from this the volume which the gas would have occupied if from an infinitely

<sup>1)</sup> *Comp. Comm.* N<sup>o</sup>. 50, *These Proc.* II June 1899, p. 29, and N<sup>o</sup>. 70, V, *These Proc.* IV, June 29, 1901, p. 107.

large volume at 20° C. it were reduced to a pressure of 1 atm., and it had followed the laws of the ideal gases. We then find the theoretical normal volume (at 0° C.) by means of the coefficient of pressure variation (= coefficient of dilatation) for the ideal gaseous state. As the calculations of the correction that according to Comm. N°. 71 (These Proc. IV June 29, 1901, p. 125) must be applied to the coefficient of pressure variation of pure hydrogen in order to find that coefficient for the ideal gaseous state were not finished when I began my calculations, I have adopted for this the value 0.0036625, which in Comm. N°. 71 was given as a first approximation. The corrections, however, which accordingly must be applied to the results, will certainly lie far below the degree of accuracy which I could attain in my experiments of the isothermals at high pressures.

After what has been said on the calibrations<sup>1)</sup>, the measurement of the normal volume and the reduction to the theoretical normal volume I can confine myself to a short note on the measurement of the volumes. The top and the base of the mercury were read with an eye-glass, parallax was avoided in the way described before (Comp. this Comm, I p. 533). In this manner 0.1 mm. could be read. We assumed that the mercury meniscus in the graduated stem of the experimental tube has the form of a spherical segment, hence by multiplication of the bore by half the height the volume may be found with a sufficient degree of accuracy, our method of reading considered. When the mixtures split into two phases, the position of the liquid meniscus was also read. Corrections were applied for the expansion of glass due to heat and to the inner pressure.

§ 4. *The measurement of the pressures.* The pressures were measured with a hydrogen manometer, ranging from 62 to 196 atmospheres<sup>2)</sup>.

In the first part of this Comm. (p. 532 ff.) I have discussed the calibration, in § 3 of this paper the determination of the normal volume. We need only add that the hydrogen was prepared as described in Comm. N°. 27 Zittingsversl. V, Mei 1896 p. 42.

From the means of the values of  $V_A$  and  $V_B$  of the table from which table VII forms an extract and from the normal volume

<sup>1)</sup> Comp. this Comm. I, p. 532.

<sup>2)</sup> It appeared that the manipulations of the stems of the manometer- and the piezometer tubes in the blow-pipe, as for instance the sealing of the top of the latter, had to be made with special care and the tube had to be cooled very carefully and slowly, else tensions will rise in the glass and consequently when high pressure is applied (in these experiments 140 atm. was reached, the manometer has stood 195 atms. several times) the tube will burst.

given in § 3, while the volume of the narrow capillary above between the mark and the place where it is sealed was accounted for, a table was derived. This new table gives for each division  $Q$  the density  $d_A$  of the hydrogen when the mercury reaches that division at a temperature of  $20^\circ$  C., expressed in terms of the normal density (0 C., 1 atm. 45 N.L.) as unity. For the values of  $Q$  between 25 and 50 the table increases by 0.5; hence also for the higher values of the pressure (as far as  $Q = 40$ ) the error made by interpolating linearly is less than 1 atm.

To derive from these densities the corresponding pressures we must know the isothermal of hydrogen at  $20^\circ$  C. Measurements of this have been made by SCHALKWIJK: they do not, however, exceed the density 54. An extrapolation from these observations for the densities wanted is not allowed with a view to the mean error of his determination of the  $C$  of the series of KAMERLINGH ONNES (cf. SCHALKWIJK's Thesis for the doctorate, p. 115). Observations at higher densities have been made by AMAGAT (from 100 to 3000 atms.) The isothermal for hydrogen at  $20^\circ$  C. derived from AMAGAT's data:

$$pv_{A_{20}} = 1.07252 + 0.0007194 d_A + 0.000000672 d_A^2$$

(cf. SCHALKWIJK's Thesis for the doctorate p. 121) does not agree, however, with that from SCHALKWIJK's observations. From these for instance, follows at  $d_A = 55$ :  $pv_{A_{20}} = 1.11194$  (cf. l. c. p. 124), hence  $p = 61.157$ , whereas from the isothermal given by AMAGAT we derive at  $p = 61.157$ :  $d_A = 54.897$ . SCHALKWIJK's observations have been made very carefully especially his determination of the normal volume (see Comm. N<sup>o</sup>. 70, V, These Proc. IV June 29, 1901, p. 107). If with this we compare the way in which AMAGAT has determined his normal volume (Ann. de Chimie et de Physique, t. 39, 1893, p. 83) it seems not entirely without reason if, while waiting for more accurate determinations of the isothermals of hydrogen at higher densities, we make those of AMAGAT agree with those of SCHALKWIJK by multiplying all the volumes of the former by the factor  $\frac{54.897}{55}$ .

So we obtain:

$$pv_{A_{20}} = 1.0705 + 0.000717 d_A + 0.00000067 d_A^2.$$

To test this we compare the value of  $pv_{A_{20}}$  at  $d_A = 1$ , viz.: 1.0712 resulting from it, with the value of  $pv_{A_{20}}$  which follows from the value of the coefficient of expansion according to CHAPPUIS:  $\alpha_c = 0.0036606$  1), [viz.: 1.0732. The difference is  $\frac{1}{500}$ , so that the

1) See SCHALKWIJK, Thesis for the doctorate p. 116.

equation found, which deviates from AMAGAT's observations at higher densities  $\frac{1}{500}$ , does not deviate from the observations at smaller densities by more than  $\frac{1}{500}$ .

The following term in the series of KAMERLINGH ONNES would be  $\frac{D_A}{rA^4}$ . If we derive a value of  $D_A$  from the data given in Comm. N<sup>o</sup>. 71, These Proc. IV June 29, 1901, p. 132, for hydrogen at 0°C., 15°.4C., 99°.25 C. and 200°.25 C., we find that this term for  $d_A = 150$  would yield in  $\rho r A_{20}$ : 0.0009, so that if we omit this term at the highest pressures an error of less than  $\frac{1}{1000}$  is made. As there exists already some uncertainty about the exact shape of the isothermal, I have omitted this term.

The values  $\rho r A_{20}$  calculated thus for the different values of  $d_A$  of the table mentioned at the beginning of this section, have been added to this table together with the values for  $\rho$  derived from them<sup>1)</sup>.

When the isothermal of hydrogen at the densities occurring here will be known more accurately, the pressures given here will require a correction for which the afore mentioned table may be useful.

The temperature of the manometer differed at most a few tenths of a degree from 20° C. The temperature coefficients for hydrogen at 20° C. are found from the value of  $A_{A_0}$  (given in Comm. N<sup>o</sup>. 71) of the series of KAMERLINGH ONNES and AMAGAT's values of  $B_A$  and  $C_A$  (given in SCHALKWIJK's Thesis for the doctorate, p. 120), for the temperatures 0° C., 15°.4 C. and 47°.3 C., observing the reduction mentioned to obtain the agreement with SCHALKWIJK's isothermal.

TABLE XVII.

$\rho$	$\left(\frac{\partial \rho}{\partial T}\right)_r$	$\rho$	$\left(\frac{\partial \rho}{\partial T}\right)_r$	$\rho$	$\left(\frac{\partial \rho}{\partial T}\right)_r$
200	0.714	150	0.531	100	0.349
190	0.677	140	0.494	90	0.314
180	0.640	130	0.458	80	0.279
170	0.603	120	0.422	70	0.243
160	0.567	110	0.385	60	0.208

<sup>1)</sup> This table has been given in my thesis for the doctorate.

Column  $\left(\frac{\partial p}{\partial T}\right)_r$  of table XVII gives the temperature coefficients thus found for the different pressures  $p$ .

Also a correction was applied for the difference in level of the mercury columns in the manometer and the experimental tube, for the expansion of the volume of the manometer tube caused by the inner pressure, and for the difference in capillary depression in the two tubes. For the latter a separate experiment has been made to determine the depression in a tube of the same inner bore as the manometer tube. This correction was 0.01 atmosphere.

The manometer was read in the same way as the piezometer (see p. 558). The level of the mercury in the manometer tube and the temperature of this were read before and after the reading of the meniscus and the temperature of the experimental tube. The temperature of the manometer could be read to within 0°.05.

After the isothermal determinations the hydrogen manometer was compared with the standard manometers (Comm. N°. 50, Proc. June 1899) which have been very accurately compared with the open manometer by SCHALKWIJK (Comm. N°. 67, Proc. Dec. 1900 and Jan. 1901, Comm. N°. 70, Proc. May and June 1901). To render this possible the hydrogen manometer had been constructed so that the lowest pressure which could be read on it could still be measured with the standard manometer IV<sup>1)</sup>. Table XVIII gives under the heading A the pressure as measured with the hydrogen manometer used by me, under the heading B the same pressure measured with the standard manometer.

TABLE XVIII.

A	B
64.04	64.040
64.02	64.024

Obviously the agreement is quite satisfactory. This comparison comes in the place of the determination of the normal volume after the measurements, and also of more determinations of the normal bore of the graduated stem. (Comp. p. 540). As there mentioned mean percentage difference 0.19 % is principally due to the difference

<sup>1)</sup> For the way in which this comparison has been made comp. VERSCHAFFELT, Thesis for the doctorate p. 17.

between the two determinations of the normal bore, this comparison highly improves the accuracy of the manometer.

The thermodynamical equilibrium in the experimental tube was reached by means of an electromagnetic stirring apparatus: to secure the equilibrium of pressure between the experimental tube and the manometer I waited 5 minutes after each adjustment before reading. Of each isothermal two series of observations were usually made, one beginning with the lowest and ending with the highest pressure, the other in reversed order. Only rarely the results of these two differed as much as  $\frac{1}{500}$ . To judge of this see table XIX, which relates to the isothermal for 22°.68 C. of a mixture of 0.1047 oxygen in carbon dioxide. Here  $v$  represents the volume,  $p_r$  and  $p_f$  the corresponding pressures in the two series, with a constantly rising and a constantly falling pressure respectively,  $\Delta p$  the difference,  $v_{liq,r}$  and  $v_{liq,f}$  the volumes of the liquid also in the two series,  $\Delta v_{liq}$  the difference between them.

The agreement of the pressures is satisfactory, that of the volumes of the liquid leaves to be desired. Although this is partly explained by the circumstance that the volume of the liquid cannot be read so accurately because the form of the meniscus is not so sharply determined as is the case with mercury, and parallax could not so easily be avoided as with the mercury menisci, it yet appears that, if we desire to investigate this subject more fully, more care should be taken to procure equilibrium by stirring and waiting.

§ 5. *The constancy and the measurement of the temperatures.* The manometer was surrounded by a jacket with flowing water kept at constant temperature by a thermostat, as described by SCHALKWIJK (Comm. N°. 70, Proc. May '01) with the modification in the thermoregulator described in Comm. N°. 78 (Proc. April 1902 p. 762).

In the same way the experimental tube was kept at constant temperature by means of a second thermostat. This differed from the former in the following respects:

The connection between the heating bath and the mixing bath, the mixing bath and the connection between the mixing bath and the observation bath have been insulated more carefully by means of wool, paper and felt; this was necessary because greater differences of temperature with the surrounding atmosphere occur here.

To the glass portion of the thermoregulator a side-tube with a cock is sealed on, which facilitates the admission of a quantity of mercury from a mercury reservoir, which by means of an india rubber tube is connected with that side-tube, into the thermoregulator

TABLE XIX.

$v$	$l_r$	$l_f$	$\Delta l$	$r_{1,r}$	$r_{i,f}$	$\Delta r_{1,r}$
0.012159	58.66	58.60	+0.06			
41384	60.88	60.92	-0.04			
40605	63.27	63.31	-0.04			
0.009826	65.74 <sup>s</sup>	65.77 <sup>s</sup>	-0.03			
9047	68.26	68.31	-0.05			
8269	70.90	70.94	-0.04			
7489 <sup>s</sup>	73.47	73.51	-0.04			
6712 <sup>s</sup>	76.07	76.41	-0.04			
5908 <sup>s</sup>	78.72 <sup>s</sup>			<i>b.c.</i> difference in saturation volume:		
5917 <sup>s</sup>		78.75 <sup>s</sup>	-0.03	<i>b.c.</i>	-0.000009	
5546	79.95 <sup>s</sup>	79.98 <sup>s</sup>	-0.03	0.000217	0.000180	+0.000037
5157	81.26 <sup>s</sup>	81.39 <sup>s</sup>	-0.13	397	403	- 6
4768	82.88 <sup>s</sup>	82.89 <sup>s</sup>	-0.01	612	583	+ 29
4379	84.70 <sup>s</sup>	84.76 <sup>s</sup>	-0.06	746	672	+ 47
4309		85.05			591	
4278	85.22			625		
4258		85.35			288	
4243		85.40			95	
4219	85.54			425		
4215 <sup>s</sup>	85.54			<i>e.c.</i> difference in saturation volume:		
4220 <sup>s</sup>		85.52	+0.02	<i>e.c.</i>	-0.000005	
3391 <sup>s</sup>	87.10 <sup>s</sup>	86.95 <sup>s</sup>	+0.15			
3304	90.24	90.22	+0.02			
3049	90.29 <sup>s</sup>	90.08 <sup>s</sup>	+0.21			
2752	112.63	112.71	-0.08			
2612	124.64	124.36	+0.28			

and hence the adjustment for different temperatures<sup>1)</sup>. The narrow part of the glass tube where the supply of gas is regulated, has

<sup>1)</sup> A similar arrangement has been described by FRIEDLÄNDER, Zeitschrift für physikalische Chemie, Bd. 38 p. 401, 1901.

been graduated in mm. over a length of 4 cm., which facilitates a finer adjustment by moving up and down the supply tube.

For temperatures higher than  $35^{\circ}$  the water streamed successively through two heating baths, each provided with a thermoregulator; the first brought the water to  $35^{\circ}$  C., the second to the desired temperature. To avoid exchange of heat with the surrounding atmosphere the last bath was coated with asbestos, except where it came into contact with the flames.

One thermoregulator had been constructed for higher temperatures, filled with xylene and goes as far as  $+90^{\circ}$  C., the other for lower temperatures was filled with benzole, of which the coefficient of expansion was determined at 0.0011 and goes from  $-40$  to  $+40^{\circ}$  C.

For temperatures below that of the water supply, the water streamed between the overflow and the heating bath through a zinc vessel insulated with felt, where small pieces of ice were continually brought in.

By leading the water back to the overflow after it has flown through the observation jacket by means of a membrane pump<sup>1)</sup> through tubes enclosed in wool, we could make measurements to about  $1^{\circ}.9$  C. For the experiments with the mixture 0.3, mentioned in § 3, we used the current of solution of calciumchloride at constant temperature, described in Comm. N<sup>o</sup>. 87, Zittingsversl. Deel XII Juni 1903 (see Pl. II of that Comm., which shows the whole arrangement with the thermostat and the observation bath).

For temperatures above  $30^{\circ}$ , and also for temperatures as much again below the temperature of the room, it appeared necessary to replace the observation bath, which first consisted of a simple glass tube, by a vacuum jacket<sup>2)</sup>. After this the difference in temperature at  $34^{\circ}$  C. over a height of 33 cm. without stirring amounted to  $0^{\circ}.02$  C. Moreover we have always stirred before each observation. The water was insulated from the copper piece with which the jacket was fastened to the steel flanged tube of the experimental tube by a layer of sulphur. This prevented the cement from softening.

In order to prevent variations of temperature of the gas compressed in the experimental tube owing to conduction of heat along the mercury column to the mercury in the compression tubes, we took care that in the observations, where the mercury meniscus was lowest the mercury column still stood over a length of 40 cms. in the jacket.

1) Comp. DE HAAS, Thesis for the doctorate fig. 1.

2) Comp. Comm. N<sup>o</sup>. 85, Versl. Deel XII Juni 1903, p. 214. The case acting as a spring was placed as low as possible to leave room for the coil which moves the electro-magnetic stirrer.

The temperature of the experimental tube was read with an eye-glass to within  $0^{\circ}.01$  on an "Einschlussthermometer", divided into  $0^{\circ}.1$ , with a scale on milkglass. From time to time this was compared at different temperatures with a similar thermometer tested at the Reichsanstalt with the air thermometer, while the variation of the zero of the latter in the mean time was accounted for and also the temporary depression of the zero, which, after the thermometer had for a long time been heated at  $48^{\circ}$  C., amounted to  $0^{\circ}.02^5$  C.

6. *Reduction of the observations.* In cases where, in contrast to the determination of the plaitpoint and the point of contact of the mixtures and the critical point of carbon dioxide, the greatest possible constancy of the temperature was not absolutely necessary, the temperature during the determination of an isothermal which lasted on an average from 3 to 4 hours was allowed to vary a few hundredths of a degree. For the reduction to one temperature, temperature coefficients for the different volumes were derived from the observations.

In the two series, one at an always increasing, the other at an always decreasing pressure, pressures were measured, corresponding to different volumes, which in the two series differed but little. Pressures were derived from them for the same volume and then the mean was found. When it appeared that these pressures agreed sufficiently (comp. § 4) we have afterwards simply taken for two corresponding points the mean of the volume and the pressure.

**Physics.** — "*Isothermals of mixtures of oxygen and carbon dioxide. IV. Isothermals of pure carbon dioxide between  $25^{\circ}$  C. and  $60^{\circ}$  C. and between 60 and 140 atmospheres.*" By W. H. KEESOM. Communication N<sup>o</sup>. 88 (4<sup>th</sup> part) from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.

§ 1. *Reason for the investigation of carbon dioxide.* Although the isothermals of carbon dioxide have been extensively investigated by AMAGAT, I have yet determined a number of isothermals together with its critical point. I was led to it by the following considerations:

1<sup>st</sup>. it was desirable that I should be able to judge of the purity of the carbon dioxide which I used for the preparation of the mixtures, and it seems that this judgment may best be derived from the increase of the vapour pressure with condensation at a stationary temperature <sup>1)</sup>:

<sup>1)</sup> Comp. Comm. N<sup>o</sup>. 79. Proc. April 1902.

2<sup>nd</sup>. difficulties had arisen about some quantities at the critical point of carbon dioxide, which are important for the theory of the mixtures. AMAGAT, for instance, had determined the critical pressure at 72.9 atm., while VERSCHAFFELT from AMAGAT's isothermals derived 73.6 atm.<sup>1)</sup> Obviously this may give rise to an error in the determination of the data of the critical point of the mixtures, if as in Comm. N<sup>o</sup>. 59<sup>2)</sup> the logarithmical systems of isothermals are shifted over each other. Moreover in Comm. N<sup>o</sup>. 75, Proc. Dec. 1901 p. 299, for  $\left(\frac{\partial\pi}{\partial r}\right)$  at the critical point from AMAGAT's isothermals: 7.3 had been derived: from his determinations of the saturated vapour pressures: 6.5. This points to an uncertainty in the determination of the critical volume. AMAGAT has determined the critical point and the vapour pressures in different apparatus and hence probably also with other carbon dioxide than the isothermals; by determining the two in the same tube with the same carbon dioxide I hoped to arrive at more certainty on these points.

3<sup>rd</sup>. By comparing the isothermals of the mixtures after RAVEAU's method with isothermals of carbon dioxide observed in the same experimental tube some systematical errors which might occur in the observations are eliminated from the determination of the critical data of the mixtures. In this way an error in the determination of the diameter of the graduated stem of the experimental tube would have no influence on the critical pressure and temperature of the mixture.

§ 2. In the following tables  $v$  is the volume expressed in terms of the theoretical normal volume,  $p$  the pressure in atmospheres ( $0^{\circ}$  C.,  $45^{\circ}$  Northern latitude),  $v_{liq}$  the volume of the liquid. The points of the beginning and the end of the condensation are marked by the letters  $bc$  and  $ec$ . For the point  $bc$  we adopted the point where after having decreased the volume there appeared for the first time with proper stirring a liquid "Schlier" on the wall, or after having increased the volume with proper stirring only such "Schlier" remained. These two points agreed sufficiently. The point  $ec$  could be observed sharply, as with a small variation of the volume the last part of the phase disappeared or reappeared. Especially here, however, phenomena of retardation had to be avoided by forcible stirring.  $V_{th,N}$  stands for the theoretical normal volume, the meaning of  $\Delta K_{50}$  is explained in the 2<sup>nd</sup> part of this Comm., p. 552.

1) Comp. Comm. N<sup>o</sup>. 55, Proc. April 1900.

2) Proc. Sept. 1900.

*First carbon dioxide.*Before the measurements:  $V_{thN} = 71.020^s$  c.c.

$$A_{K_{20}} = 1.00570$$

a. Isothermal of  $25^{\circ}.55$  C.

No.	$v$	$p$	$pv$	$v_{liq}$
1	0.008573	63.12	0.5411 <sup>s</sup>	
2	7812	64.36	5028	<i>lc</i>
3	7046	64.42	4539	0.000420
4	6227 <sup>s</sup>	64.41	4011	859
5	5504	64.41	3545	0.001276
6	4837	64.40	3115	1664
7	4068	64.39	2619	2088
8	3205	64.42	2065	2597
9	3085	64.37	1986	2652
10	2869	64.41	1848	<sup>2)</sup>
11	2738	64.43 <sup>1)</sup>	1802 <sup>s</sup>	<i>ec</i>
12	2645	70.91	1876	
13	2520	80.65 <sup>s</sup>	2033	
14	2438	92.97	2267	
15	2366	105.79	2503	
16	2309	122.55 <sup>s</sup>	2830	
17	2270	138.42	3142	

1) We shall later revert again to the purity of the carbon dioxide, as it appears from the increase of pressure at the condensation.

2) Here the liquid meniscus reached the part of the tube where through the sealing in the blow-pipe the marks no longer were visible.

*b.* Isothermal of 28°.15 C.

No.	<i>v</i>	<i>p</i>	<i>pv</i>	<i>v<sub>liq</sub></i>
1	0.009538	63.44	0.5924	
2	8565	65.19	5583	
3	7807 <sup>s</sup>	66.75 <sup>s</sup>	5212	
4	7030	67.99 <sup>s</sup>	4780	
5	6950	68.19	4739 <sup>s</sup>	
6	6673	68.39	4564	<i>bc</i>
7	6300	68.41	4310	0.009290
8	5502	68.41	3764	947
9	4712	68.43 <sup>s</sup>	3224 <sup>s</sup>	0.001625
10	3974	68.48	2721	2189
11	3149	68.45	2135	1)
12	3011	68.43	2060	<i>ec</i>
13	2813	72.40 <sup>s</sup>	2037	
14	2670	78.55	2097	
15	2546	89.54	2279	
16	2446	103.47	2531	
17	2360	119.61	2834	
18	2315	136.58	3161	

*c.* Bordereurve in the neighbourhood of the critical point.

Beginning condensation

End condensation

Temp.	<i>v</i>	<i>p</i>
30.05	0.005594	71.47
30.82	4833	72.72 <sup>s</sup>

Temp.	<i>v</i>	<i>p</i>
30.41	0.003328	71.53
30.81	3725	72.74

*d.* Critical point :Temp. : 30.98      Pressure : 72.93      Volume : 0.00443 <sup>2)</sup>.

1) Comp. footnote to the preceding table.

2) For the determination of this comp. § 5.

*e.* Critical isothermal: (30.98° C.)

No.	$r$	$p$	$pv$
1	0.010068	63.36	0.6379
2	0.009314	65.39	0.6090
3	8582	67.22	0.5769
4	7809	69.08	0.5395
5	7031	70.73	0.4973
6	6275	71.95	0.4515
7	5483	72.74	0.3988
8	5102	72.87	0.3718
9	4777	72.93	0.3484
10	4403	72.94	0.3211
11	4254	72.98	0.3104
12	3959	72.96	0.2888
13	3656	72.99	0.2669
14	3296	73.53	0.2423
15	3230	73.89	0.2387
16	3051	75.43	0.2302
17	2862	79.43	0.2273
18	2721	86.10	0.2343
19	2593	95.70	0.2482
20	2509	106.18	0.2664
21	2435	119.35	0.2906
22	2362	138.65	0.3275

*f.* Isothermal of 31.89° C.

No.	$r$	$p$	$pv$
1	0.010086	63.87	0.6442
2	0.009314	65.99	0.6147
3	8570	67.94	0.5823
4	7771	70.03	0.5442
5	7017	71.68	0.5030
6	6267	73.03	0.4577
7	5528	73.94	0.4087
8	5147	74.24	0.3799
9	4742	74.44	0.3520
10	4364	74.56	0.3254
11	3942	74.69	0.2944
12	3610	75.00	0.2707
13	3228	76.20	0.2460
14	2883	82.02	0.2365
15	2717	89.90	0.2443
16	2523	99.77	0.2587
17	2503	111.45	0.2790
18	2439	122.79	0.2995
19	2377	136.71	0.3244

## g. Isothermal of 34°.02 C.

No.	$v$	$p$	$pv$
1	0.010067	65.18	0.6562
2	0.009337	67.29 <sup>5</sup>	0.6283
3	8560	69.49	0.5948
4	7791	71.64	0.5581 <sup>5</sup>
5	7023 <sup>5</sup>	73.65	0.5173
6	6255	75.74	0.4712
7	5529 <sup>5</sup>	76.60 <sup>5</sup>	0.4236
8	4672	77.57 <sup>5</sup>	0.3624
9	3971	78.38 <sup>5</sup>	0.3113
10	3243	81.41	0.2630 <sup>5</sup>
11	2955	86.46	0.2546
12	2746	95.02	0.2609
13	2614	105.95	0.2770
14	2510	119.53	0.3000
15	2426	136.66	0.3316

## h. Isothermal of 37°.09 C.

No.	$v$	$p$	$pv$
1	0.010863	64.56	0.7013
2	10093	66.90	0.6752
3	0.009339	69.29	0.6471
4	8554	71.73	0.6135 <sup>5</sup>
5	7810	74.41	0.5788
6	7059	76.40	0.5394
7	6287	78.58 <sup>5</sup>	0.4940
8	5525 <sup>5</sup>	80.47	0.4446
9	4770	82.41	0.3917
10	4011	83.89	0.3365
11	3230	88.89	0.2871
12	2799	103.08	0.2885
13	2609	119.27	0.3112
14	2495	136.01	0.3393

*Second carbon dioxide* <sup>1)</sup>.

Before the experiments:  $V_{thN} = 69.647$  c.c., weight 2

After .. .. 69.629 .. .. 1

Mean 69.641 ..

## i. Isothermal of 41°.95 C.

No.	$v$	$p$	$pv$
1	0.011546	64.85	0.7487
2	10794 <sup>5</sup>	67.28	0.7262 <sup>5</sup>
3	10047	69.81	0.7014
4	0.009211	72.78	0.6704
5	8486	75.48	0.6405
6	7640	78.57	0.6003
7	6915	81.31	0.5622 <sup>5</sup>
8	6181	84.04	0.5194 <sup>5</sup>
9	5320	87.18	0.4638
10	4530	90.13	0.4082 <sup>5</sup>
11	3778	94.10	0.3555
12	3087	105.01	0.3242
13	2817	117.96	0.3323
14	2642	134.85	0.3563

## k. Isothermal of 48°.10 C.

No.	$v$	$p$	$pv$
1	0.012311	65.20	0.8027
2	11572	67.69	0.7833
3	10787 <sup>5</sup>	70.52	0.7607
4	0.009970	73.61	0.7339
5	9232	76.61	0.7073
6	8442	80.07	0.6769
7	7678	83.38	0.6402
8	6899	87.07	0.6007
9	6118	90.90	0.5561
10	5380	94.78	0.5099
11	4570	99.62	0.4552
12	3823	105.50	0.4033
13	3129 <sup>5</sup>	119.38	0.3736
14	2864	135.56	0.3883

<sup>1)</sup> Because the experimental tube has broken, the first quantity was lost. As, however, the fracture occurred below the graduated portion of the stem, the advantage mentioned in § 1, sub 3 remained.

*l.* Isothermal of 57°.75 C.

No.	<i>v</i>	<i>p</i>	<i>P</i>
1	0.013174	66.27	0.8730
2	42356	69.20	0.8550
3	41586	72.18	0.8363
4	40807 <sup>3</sup>	75.42	0.8151
5	40009 <sup>2</sup>	78.99	0.7906
6	0.009271	82.49	0.7648
7	8482	86.62	0.7347
8	7668	91.16	0.6990
9	6930	95.73	0.6638
10	6113	101.32	0.6194
11	5272	107.06	0.5751
12	4596	114.45	0.5260
13	3795	126.10	0.4786
14	2424 <sup>2</sup>	135.81	0.4647

§ 3. To simplify later calculations I have calculated for the isothermals *e*, *f*, *g*, *h*, *i*, *k*, *l* the values of *pv* for regularly increasing densities  $\left(\frac{1}{v}\right)$ . Therefor each value has been interpolated from 4 points derived directly from observation; only for the extreme values we have interpolated between 3 points<sup>1)</sup>. So we find the values given

<sup>1)</sup> For this we used the formula of LAGRANGE, which may be easily written in the following form:

$$P = P_2 + (P_3 - P_2) \frac{d - d_2}{d_3 - d_2} + (P_1 - P_1') \frac{(d - d_2)(d - d_3)(d - d_4)}{(d_1 - d_2)(d_1 - d_3)(d_1 - d_4)} + (P_4 - P_4') \frac{(d - d_1)(d - d_2)(d - d_3)}{(d_4 - d_1)(d_4 - d_2)(d_4 - d_3)},$$

where

$$P_1' = P_2 + (P_3 - P_2) \frac{d_1 - d_2}{d_3 - d_2},$$

$$P_4' = P_3 + (P_3 - P_2) \frac{d_4 - d_3}{d_3 - d_2}.$$

*P* represents *pv*, while  $\frac{1}{v}$  is represented by *d*. Supposing that *d* lies between *d*<sub>2</sub> and *d*<sub>3</sub>, the two last terms of *P* become relatively small and they may be easily calculated with a sliding-rule.

in table XX; the first column gives the different densities (expressed in terms of the theoretical normal density), the following columns the values of  $\rho v$  belonging to it, each time for the temperature mentioned at the head of the column.

TABLE XX.  
Isothermals of carbon dioxide.

$\frac{1}{v}$	30.98°	31.89°	34.02°	37.09°	41.55°	48.40°	57.75°
80							0.8583
100	0.6355	0.6411	0.6538	0.6719	0.6997	0.7340	0.7703
120	0.5653	0.5715	0.5844	0.6036	0.6335	0.6712	0.7285
140	0.5037	0.5094	0.5240	0.5440	0.5746	0.6135	0.6743
160	0.4499	0.4566	0.4708	0.4918	0.5237	0.5640	0.6273
180	0.4039	0.4106 <sup>s</sup>	0.4254	0.4466	0.4796	0.5212	0.5864
200	0.3646	0.3716	0.3863	0.4081	0.4416 <sup>s</sup>	0.4847	0.5521
220	0.3314	0.3387	0.3494	0.3754	0.4094	0.4536	0.5226 <sup>s</sup>
240	0.3041	0.3109	0.3226	0.3477	0.3819 <sup>s</sup>	0.4264	0.4991
260	0.2806	0.2875	0.3021	0.3243 <sup>s</sup>	0.3567 <sup>s</sup>	0.4048	0.4812
280	0.2611	0.2680	0.2825 <sup>s</sup>	0.3052	0.3423 <sup>s</sup>	0.3872	0.4692
300	0.2448	0.2521	0.2677	0.2915 <sup>s</sup>	0.3302	0.3763	
320	0.2333	0.2410	0.2590	0.2835	0.3245 <sup>s</sup>	0.3737	
340	0.2273	0.2321	0.2554 <sup>s</sup>	0.2863	0.3255	0.3817	
360	0.2305	0.2401	0.2588	0.2900	0.3362		
380	0.2427	0.2530	0.2742	0.3073			
400	0.2690	0.2800	0.3031	0.3376			
420	0.3199 <sup>s</sup>	0.3230					

§ 4.  $v_{liq.}$  was reduced to the same temperature for the isothermals  $a$  and  $b$  in the following way: From the height of the liquid meniscus we directly derived the volume of the vapour phase:  $v_{vap.}$  If  $v_1$  is the specific volume of the existent liquid phase,  $v_2$  the specific volume of the vapour (as unity we always have here the theoretical normal volume), we find:

$$\frac{dv_{vap.}}{dT} = - \frac{v_{vap.}}{v_2 - v_1} \left( \frac{v_1}{v_2} \frac{dr_2}{dT} - \frac{v_2 - v_1}{v_2 - v_1} \frac{dv_1}{dT} \right).$$

After the vapour volumes have thus been reduced to one temperature, the liquid volumes are derived from this. We have assumed in this that  $v_1$  and  $v_2$  are functions of the temperature  $T$  only and not also of  $v$ , as DE HEEN and others think. On this supposition we can derive  $v_1$  and  $v_2$  from each pair of observations of  $v_{liq}$  at different  $v$  and at the same temperature. The values calculated thus have been combined in table XXI together with those derived directly from observation.

TABLE XXI.

Isothermal of 25°.55 C.			Isothermal of 28°.15 C.		
Nrs.	$v_1$	$v_2$	Nrs.	$v_1$	$v_2$
2		0.007812	6		0.006673
3 and 7	0.002799	7736	7 and 9	0.003043	6680
4 and 8	2819	7722	8 and 10	2998	6709
5 and 9	2809	7747	12	3011	
11	2798				
mean	0.0028035	0.0077735	mean	0.003016	0.006684

We see that no regular variation in the values of  $v_1$  and  $v_2$  can be remarked, so that this justifies with regard to these experiments our assumption of the dependence of  $v_1$  and  $v_2$  on the temperature only.

In the calculation of the mean values of  $v_1$  and  $v_2$  in table XXI we have accorded the same weight to the value borrowed directly from observation as to the mean of the values derived from the other observations.

§ 5. For the determination of the critical point the following may serve: The thermostat was adjusted at a few hundredths of a degree below the critical temperature (the temperature above which no stationary meniscus is observed). By letting a small quantity of water of higher temperature into the mixing bath, the experimental tube was brought to a few hundredths of a degree above the critical temperature, and the substance was well stirred. Then the temperature falls very slowly. If the volume lies between certain limits, the following phenomena may be seen: A blue mist is formed which

at a definite place becomes denser and denser<sup>1)</sup>. At a given moment "striae" appear, the substance boils and rains, a meniscus is formed. From the very first, the latter is perfectly sharp and flat, it remains at the same place also after stirring. The temperature was observed immediately after the appearance of the striae, then the pressure and the volume and then the temperature was determined again. So we obtain the pressure for one or a few hundredths of a degree below the critical temperature. For this a correction has been applied.

If we allow the temperature to rise, we still see a meniscus during a considerable length of time after the temperature in the bath has risen to a few hundredths of a degree above the critical temperature. It disappears immediately, however, when we stir. Hence this is no phenomenon of equilibrium.

So we could derive the temperature and the pressure directly from observation. For the volume this was not possible, as owing to the effect of gravitation the phenomena described above occur at different volumes, so for instance in my observations with a volume: 0.003924 (stirrer below), where the meniscus appeared in the immediate neighbourhood of the top of the tube, and with a volume 0.004281 (stirrer above) where the meniscus appeared 1 mm. above the mercury.

The method generally used for the determination of the critical volume consists in determining some liquid and vapour densities at temperatures below the critical, and then using the rule of the rectilinear diameter of CALLETET and MATHIAS. To this end we have drawn on a diagram the densities resulting from the data of § 4, table XXI and § 2,  $c$ , as a function of the temperature, and the diameter has been drawn on it. A deviation from the rectilinearity could not be stated with certainty. For the critical density, expressed in terms of the theoretical normal density we derive from this diagram 239, hence for the critical volume 0.00418.

Another method is this: At the critical point  $\left(\frac{dp}{dT}\right)_{\text{crit.}} = \left(\frac{\partial p}{\partial T}\right)_c$  (for the proof see for instance Comm. N<sup>o</sup>. 75).

To determine  $\left(\frac{dp}{dT}\right)_{\text{crit.}}$  we have combined in table XXII under  $O$  the vapour pressures resulting from § 2; for the temperatures 25°.55 C and 28°.15 C we have taken the means from the different values for the pressure.

<sup>1)</sup> If the temperature is kept constant, the mist during a considerable length of time (say 10 minutes) does not change to the eye.

TABLE XXII.

Temp.	O.	C.	O—C.
25.55	64.40	64.41	+0.01
28.45	68.43	68.43	0.00
30.05	71.45	71.44	-0.01
30.82	72.72	72.67	-0.05
30.98	72.93		

If we calculate for the different values the coefficient  $f'$  for VAN DER WAALS'S formula<sup>1)</sup>:

$$\log \frac{p}{p_k} = f' \frac{T - T_k}{T},$$

we find with increasing temperature regularly decreasing values of  $f'$ . If in the development in powers of  $\frac{1}{T}$  we take one term more, so that we arrive at the formula:

$$\log \frac{p}{p_k} = \frac{T - T_k}{T} \left( f' + g \frac{T_k - T}{T} \right),$$

and we calculate the values of  $f'$  and  $g$  which give the best agreement, we find very nearly  $g = f'$ . Then I have put:

$$\log \frac{p}{p_k} = f' \frac{(T - T_k) T_k}{T^2}$$

and found  $f' = 2.914^5$ . By means of this we obtain the values for  $p$  given in column C. The agreement is quite satisfactory, only for the temperature 30°.82 C. there is a considerable deviation: the same is also found in the comparison of the saturation volumes so that here we have probably to do with an error of observation.

From this we find at the critical point:

$$\left( \frac{dp}{dT} \right)_{\text{crit.}} = 1.610.$$

From the determinations of the isothermals we cannot with certainty derive a definite variation of  $\left( \frac{\partial p}{\partial T} \right)_v$  at the same volume with the temperature, as may be best derived from table XX. Therefore I have derived  $\left( \frac{\partial p}{\partial T} \right)_v$  for the different densities from the isothermals of 30°.98 C. and 48°.10 C. and found the following values:

<sup>1)</sup> Continuität I p. 158.

TABLE XXIII.

$\frac{1}{v}$	$\left(\frac{\partial p}{\partial T}\right)_v$	$\frac{1}{v}$	$\left(\frac{\partial p}{\partial T}\right)_v$	$\frac{1}{v}$	$\left(\frac{\partial p}{\partial T}\right)_v$
100	0.581	200	1.403	300	2.304
120	0.742	220	1.570	320	2.624
140	0.898	240	1.715	340	3.066
160	1.066	260	1.886		
180	1.233	280	2.062		

If from this we interpolate in the same way as in § 3 we find that  $\left(\frac{\partial p}{\partial T}\right)_v = 1.610$  for the density 225.50, to which belongs the volume: 0.00443.

This value does not agree with that derived above from the densities. The difference is larger than can be ascribed to the errors in the observation. The deviation is in the same sense as follows from AMAGAT's experiments. The following might serve as an explanation of this difference:

According to a remark of Prof. KAMERLINGH ONNES from whom a new paper on the cause of the deviations near the critical point may be expected (comp. Comm. N<sup>o</sup>. 74, Arch. Néerl. série II, t. VI, p. 887) the appearance of the mist in the neighbourhood of the critical point seems to indicate that a part of the substance condenses round numerous centra equally distributed over the whole space. That only in this area this appears so distinctly, might be ascribed to the circumstance that here small forces are sufficient to cause great variations of density. These condensations might have a perceptible influence for instance on the saturation volume although the variation of the pressure would not become perceptible in consequence of it.

In a comparison of mixtures with pure substances according to the law of corresponding states we must disregard those condensations, as they do not occur at corresponding points (in mixtures near the plaitpoint). Hence our purpose will probably be served best if we adopt for the critical volume: 0.00443, as this value according to a thermodynamical relation results from determinations not so near to the critical point, and where therefore particular phenomena which occur in its immediate neighbourhood have played no part.

The following quantities are further found at the critical point, which are necessary for the comparison of the observations with the theoretical results of Comms. N<sup>o</sup>. 75 and N<sup>o</sup>. 81 :

$$C_4 = \frac{T_k}{T_0 p_k v_k} = 3.15,$$

$$\frac{T_k}{p_k} \left( \frac{dp}{dT} \right)_k = 6.712.$$

$$\left( \frac{\partial^2 p}{\partial T \partial v} \right)_k = -422, \text{ hence } C_4 \frac{v_k T_k}{p_k} \left( \frac{\partial^2 p}{\partial T \partial v} \right)_k = -26.9.$$

Here, in agreement with the value of the coefficient of expansion for the ideal gaseous state accepted in this Comm. III, p. 558 we have put:  $T_0 = 273.04$ .

**Physics.** — *“Isothermals of mixtures of oxygen and carbon dioxide. V. Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide”*. By W. H. KEESOM. Communication N<sup>o</sup>. 88 (5<sup>th</sup> part) from the Physical Laboratory at Leiden by Prof. KAMERLINGH ONNES.

(Communicated in the meeting of October 31, 1903.)

§ 1. The following sections contain the tables about two mixtures of carbon dioxide and oxygen. For the meaning of  $v$ ,  $p$ ,  $v_{liq}$ , and the determination of the *b.c.*- and the *e.c.*-points I refer to this Comm. IV § 2. Of the end condensation point it should be remarked that over a definite area below and above the plaitpoint temperature the meniscus, in consequence of the effect of gravitation, disappeared in the tube.

The data about the plaitpoint were derived directly from the experiment. On the phenomena near the plaitpoint I find the following remarks among my notes of the observations: When the volume increases from the homogeneous (liquid) state a blue mist gradually forms itself. As the volume increases (small variations at a time) this becomes denser. If the volume increases still more, layers of different degrees of refrangibility suddenly appear, which quickly move among themselves. When we stir, however, they still dissolve into the thickening blue mist. At a given moment, after the volume has been increased again a little, these layers begin to concentrate towards the middle of the tube, at the top and at the bottom it

becomes clear, small bubbles or drops are seen to move from below and from above towards a certain point in the tube. At last a meniscus appears there. This remains at that place. The temperature at which these phenomena were observed was adopted as the plaitpoint-temperature of the mixture considered, the volume and the pressure as plaitpoint volume and pressure.

If the temperature is a little higher, the meniscus appears lower in the tube. The exact point where it appears cannot be observed with certainty: drops are seen to move from above to below, and bubbles from below to above more and more regularly towards one place; at this place the meniscus will appear, but this place is rising already before the meniscus has properly formed itself. When it is formed, it generally still rises. If the temperature is still higher the meniscus is distinctly seen to rise from the bottom of the tube. At the lower end a quantity of liquid is gathered by the drops which fall from the top to the meniscus. The same holds, *mutatis mutandis*, for temperatures below the plaitpoint temperature.

Of the data about the point of contact only the temperature could accurately be (to within  $0^{\circ}.01$ ) derived from the experiment. To determine the pressure some points at the beginning and at the end of the condensation to within  $0^{\circ}.1$  of the point of contact were observed; they were drawn and the point where the tangent is at right angles with the axis of temperature was found. This gave the pressure of the point of contact with sufficient accuracy. Then the point of contact volume was deduced from the isothermal.

The molecular proportion of oxygen will be represented by  $x$ ,  $V_{thN}$  is the theoretical normal volume, for the meaning of  $A_{K_{20}}$  comp. this Comm. II p. 552.

§ 2. *First mixture of carbon dioxide and oxygen.*

$$x = 0.1047.$$

Before the measurements:  $V_{thN} = 69.743$  cc.

After     ,,     ,,                             69.725     ..

mean: 69.734     ..

a. Border curve.

Beginning condensation.

Temp.	$v$	$p$
17.53 <sup>s</sup>	0.008552	66.08
17.63	8483	66.40
19.48	7708	69.48
20.19	7362	71.59
20.28	7288	71.94
21.48	6709	74.85
22.06	6456	76.24
22.38	6098	77.85
22.83	5860	79.14
22.87	5822	79.26
22.98	5697	79.95
23.23	5366	81.46

End condensation.

Temp.	$v$	$p$
11.68	0.002597	85.52
14.78	2757	87.09
17.52 <sup>s</sup>	2949	88.25
17.68	2986	88.29
19.38	3195	88.46 <sup>s</sup>
20.19	3292	88.35
20.28	3323	88.35
21.48	3664	87.35
22.09	3880	86.58
22.43	4069	86.03
22.80	4301	85.34
22.88 <sup>s</sup>	4324	85.12
22.98	4441	84.90
23.18	4663	84.16

b. Isothermal of 17°.60 C.

No.	$v$	$p$	$pv$	$vliq.$
1	0.011384	58.35	0.6642	
2	10695	60.46	0.6412	
3	0.009826	62.62	0.6153	
4	9047	64.84	0.5866	
5	8503	66.24	0.5632 <sup>s</sup>	<i>bc</i>
6	7489 <sup>s</sup>	67.85	0.5182	0.000338
7	6712 <sup>s</sup>	69.54	0.4668	571
8	6108	71.12	0.4344	826
9	5935	71.65	0.4252 <sup>s</sup>	879
10	5385	73.39	0.3952	0.001105
11	5157	74.26	0.3830	1194
12	4486 <sup>s</sup>	77.12	0.3460	1502
13	4379 <sup>s</sup>	77.68	0.3402	1556
14	3482	83.35	0.2902	2189
15	2954	88.30	0.2608	<i>ec</i>
16	2848	91.71 <sup>s</sup>	0.2612	
17	2719 <sup>s</sup>	97.38	0.2648	
18	2572	109.13	0.2807	
19	2466	123.34	0.3042	

## c. Isothermal of 20°.29 C.

No.	$v$	$p$	$pv$	$v_{liq.}$
1	0.011699	58.86	0.6886	
2	11384	59.72	0.6798	
3	10605	61.94	0.6569	
4	0.009826	64.31	0.6319	
5	9047	66.62	0.6027	
6	8900	67.15	0.5976	
7	8269	69.04	0.5769	
8	7490	71.41	0.5348	
9	7291	71.98	0.5248	<i>lc</i>
10	6713	73.07	0.4905	0.000267
11	5935	75.32	0.4470	596 <sup>s</sup>
12	5157	77.94	0.4019 <sup>s</sup>	938
13	4468	80.88	0.3614	0.001360
14	4379	81.39	0.3564	1445
15	3640	85.85	0.3125	2230
16	3501	86.91	0.3043	2540
17	3335	88.28	0.2944	<i>cc</i>
18	3132	91.50	0.2866	
19	2959	95.64	0.2830	
20	2897	97.76	0.2832	
21	2759	104.46	0.2882 <sup>s</sup>	
22	2613	114.89	0.3002	
23	2527	125.12 <sup>s</sup>	0.3162	

## d. Plaitpoint isothermal (21°.99 C.).

No.	$v$	$p$	$pv$	$v_{liq.}$
1	0.012159	58.36	0.7036	
2	11384	60.52	0.6889	
3	0.009826	65.32	0.6419	
4	8269	70.37	0.5819	
5	6713	75.37	0.5052 <sup>s</sup>	
6	6400	76.42	0.4891	<i>lc</i>
7	5935	77.64	0.4608	0.000210
8	5157	80.34	0.4143	638
9	4379	83.76	0.3668	0.001169
10	3878	86.60	0.3358	<i>pp</i>
11	3613	88.74	0.3206	
12	3054	97.41 <sup>s</sup>	0.2966	
13	2769	109.26	0.3025	
14	2598	123.75	0.3215	

## e. Isothermal of 22°.68 C.

No.	$v$	$p$	$p^v$	$v_{liq}$
1	0.012159	58.63	0.7129	
2	11384	60.90	0.6933	
3	10605	63.29	0.6712	
4	0.009826	65.76	0.6461 <sup>s</sup>	
5	9047	68.28 <sup>s</sup>	0.6178	
6	8269	70.92	0.5865	
7	7489 <sup>s</sup>	73.49	0.5504	
8	6712 <sup>s</sup>	76.09	0.5108	
9	5913	78.74	0.4656	<i>bc</i>
10	5546	79.97	0.4435	0.000198 <sup>s</sup>
11	5157	81.33	0.4194	400
12	4768	82.89	0.3952	597 <sup>s</sup>
13	4379	84.73 <sup>s</sup>	0.3711	709
14	4309	85.05	0.3664 <sup>s</sup>	591
15	4278	85.22	0.3646	625
16	4258	85.35	0.3634	288
17	4243	85.40	0.3623 <sup>s</sup>	95 <sup>1)</sup>
18	4219	85.54	0.3609	125
19	4218	85.53	0.3608	<i>ec</i>
20	3991 <sup>s</sup>	87.03	0.3474	
21	3604	90.23	0.3252	
22	3049	99.49	0.2025	
23	2752	112.67	0.3101	
24	2612	124.50	0.3252	

1) To explain the irregular course of  $v_{liq}$  here, we refer to this Comm. III, p. 562, while we remark that the variations of  $v_{liq}$  with the temperature and with the volume become very large in this area, so that a small error in the latter may give rise to a large error in the value of  $v_{liq}$ .

*f.* Point of contact isothermal (23°.29 C.). *g.* Isothermal of 25°.20 C.

No.	<i>v</i>	<i>p</i>	<i>pv</i>	No.	<i>v</i>	<i>p</i>	<i>pv</i>
1	0.012159	58.95	0.7168	1	0.012159	59.81	0.7272 <sup>s</sup>
2	41785	60.04	0.7075 <sup>s</sup>	2	41384	62.14	0.7074
3	41384	61.21	0.6668	3	40605	64.59	0.6850
4	40605	63.59	0.6744	4	0.009826	67.23	0.6606
5	0.009826	66.09	0.6494	5	9047	69.97	0.6320
6	9047	68.70	0.6215	6	8269	72.78	0.6018
7	8269	71.34	0.5899	7	7490	75.69	0.5669
8	7490	74.04	0.5545	8	6712 <sup>s</sup>	78.59	0.5276
9	6712 <sup>s</sup>	76.71	0.5149	9	5935	81.69	0.4848
10	5935	79.48	0.4717	10	5156 <sup>s</sup>	84.85	0.4376
11	5156	80.80	0.4481	11	4768	86.61	0.4130
12	5157	82.23	0.4241	12	4379	88.70	0.3885
13	4768	83.78	0.3995	13	3.91 <sup>s</sup>	91.40	0.3648
14	4379	85.88	0.3761	14	3609	94.97	0.3427
15	3991	87.97	0.3511	15	3229	101.13	0.3266
16	3605	91.26	0.3290	16	2846	114.98	0.3273
17	3046	101.03	0.3077	17	2710	124.35	0.3370
18	2791 <sup>s</sup>	112.40	0.3138				
19	2646	124.08	0.3283				
Point of contact:							
	0.005005	82.83					

This mixture has been prepared in a simpler mixing apparatus than that referred to in this Comm. II § 3, and the pressures are measured with an air manometer and then reduced to the indications of the hydrogen manometer used later, as said in III § 3.

Of the border curve it may be remarked that below 19°.38 C. the end condensation pressure decreases at a falling temperature, which has not been observed by VERSCHAFFELT in mixtures of carbon dioxide and hydrogen at the temperatures at which he observed.

Between the plaitpoint- and the point-of-contact-temperature there was retrograde condensation of the first kind (temporary liquid phase),

§ 3. *Second mixture of carbon dioxide and oxygen.*

$$x = 0.1994$$

$$A_{K_{20}} = 1.00413.$$

Before the experiments:  $V_{thN} = 69.608$  cc<sup>3</sup>.

After „ „ 69.555 „

mean: 69.581<sup>5</sup> „

*a.* Border curve.

Beginning condensation.				End condensation.			
No.	Temp.	$v$	$p$	No.	Temp.	$v$	$p$
1	10.06	0.009233 <sup>5</sup>	66.35	1	10.09	0.003205	102.48 <sup>5</sup>
2	12.15 <sup>5</sup>	8190 <sup>5</sup>	71.57	2	12.20	3633	100.05 <sup>5</sup>
3	14.12 <sup>5</sup>	7125 <sup>5</sup>	77.29	3	14.11	3994 <sup>5</sup>	97.37 <sup>5</sup>
4	16.01	5803	86.02	4	16.00	4784	92.57
5	16.23	5530	87.84	5	16.22	5156	90.55

*b.* Isothermal of 9° 62 C.

No.	$v$	$p$	$pv$	$v_{liq.}$
1	0.009795	64.05	0.6274	
2	9412	65.36	0.6152	<i>bc</i>
3	8792	66.89	0.5881	0.000124
4	7948	69.16	0.5497	308
5	7147	71.79	0.5131	470
6	6404	74.92	0.4798	672
7	5500	79.65	0.4381	909
8	4811	84.23	0.4052	0.001122
9	4022	91.55	0.3682	1464
10	3338	100.07	0.3340	2221
11	3164	102.67	0.3248	<i>cc.</i>
12	2874	112.50	0.3233	
13	2742	121.35	0.3327	
14	2699	125.18	0.3379	
15	2632	129.33	0.3404	
16	2581	135.67	0.3502	

## c. Isothermal of 11°.35 C.

No.	$v$	$p$	$p^v$	$v_{liq.}$
1	0.010341	63.46	0.6562	
2	0.009505	66.25	0.6298	
3	8763	68.90 <sup>s</sup>	0.6038	
4	8629	69.37	0.5986	<i>bc</i>
5	7950	70.95	0.5640 <sup>s</sup>	0.000217
6	7203	73.53 <sup>s</sup>	0.5297	384
7	6396	77.02	0.4926	573
8	5608	81.14	0.4550	781
9	4829	86.40	0.4172	0.001097
10	4097	92.84	0.3804	1376
11	3712	96.79	0.3593	1707
12	3446	100.08	0.3449	2336
13	3397	100.89	0.3427	<i>ec</i>
14	3280	103.21	0.3385	
15	3028	110.48	0.3345	
16	2853	119.11	0.3398	
17	2718	128.44	0.3491	
18	26.4	137.56	0.3605	

## d. Plaitpoint isothermal (12°.51 C.).

No.	$v$	$p$	$p^v$	$v_{liq.}$
1	0.010259	64.42	0.6609	
2	0.009570	66.77	0.6390	
3	8741	69.74	0.6096	
4	8040	72.27	0.5811	<i>bc</i>
5	7197	75.46	0.5409	0.000201
6	6378	78.56	0.5010 <sup>s</sup>	439
7	5597	82.66	0.4627	674
8	4772	88.24	0.4211	0.001041
9	3981	95.61	0.3806	1360
10	3606	99.65	0.3593	<i>pp</i>
11	3299	105.38	0.3476 <sup>s</sup>	
12	3057	112.34	0.3434	
13	2870	121.71	0.3493	

*e.* Isothermal of 14°.04 C.

No.	<i>v</i>	<i>p</i>	<i>pv</i>	<i>v</i> <sub>liq.</sub>
1	0.010318	65.06	0.6713	
2	0.009504	67.91	0.6454	
3	8726	70.87	0.6184	
4	7926	74.06	0.5870	
5	7272	76.79	0.5584	<i>bc</i>
6	7095	77.46	0.5496	0.000043
7	6337	80.59	0.5107	0.000265
8	5694	84.05	0.4786	457
9	4761	90.15	0.4292	786
10	4402	93.16	0.4101	888
11	4066	96.35	0.3918	933
12	3947	97.55	0.3850	<i>cc</i> 1)
13	3700	100.97	0.3736	
14	3287	109.15	0.3588	
15	3002	118.66	0.3562	
16	2823	128.20	0.3619	

*f.* Isothermal of 15°.41 C.

No.	<i>v</i>	<i>p</i>	<i>pv</i>	<i>v</i> <sub>liq.</sub>
1	0.010276	66.02	0.6784	
2	0.009515	68.77	0.6543 <sup>s</sup>	
3	8763	71.71	0.6284	
4	7991	74.91	0.5986	
5	7159	78.62	0.5628	
6	6435	82.05	0.5280	<i>bc</i>
7	5971	84.32 <sup>s</sup>	0.5035	0.000139
8	5604	86.34	0.4838	228
9	5229	88.71	0.4639	327
10	4907	90.31	0.4515	367
11	4844	91.44	0.4429	387
12	4667	92.81	0.4331	361
13	4538	93.84	0.4258	273
14	4460	94.43	0.4211 <sup>s</sup>	164
15	4419	94.87	0.4192	<i>cc</i>
16	4045	98.88	0.4000	
17	3692	103.36	0.3816	
18	3253	113.06	0.3678	
19	3008	122.03	0.3671	
20	2821	133.17	0.3757	
21	2732	141.72	0.3872	

1) Here we also had retrograde condensation of the first kind, although this does not appear from the values given.

*g.* Point of contact isothermal (16°.27 C.). *h.* Isothermal of 17°.66 C.

No.	$v$	$p$	$pv$
1	0.010312	66.34 <sup>5</sup>	0.6841 <sup>5</sup>
2	0.009519	69.28	0.6595
3	8701	72.58	0.6315
4	7955	75.77	0.6028
5	7163	79.37	0.5685
6	6389	83.20	0.5316
7	5934	85.31	0.5105
8	5592	87.57	0.4897
9	5228	89.80	0.4695
10	4824	92.72	0.4473
11	4434	96.05	0.4259
12	4031	100.54	0.4053
13	3647	106.67	0.3888
14	3284	114.28	0.3753
15	3053	122.29	0.3734
16	2857	133.27 <sup>5</sup>	0.3808
17	2759	140.71	0.3832
Point of contact:			
	0.005322	89.20	

No.	$v$	$p$	$pv$
1	0.010273	67.26	0.6910
2	0.009510	70.17	0.6673
3	8683	73.60	0.6391
4	7920	76.98	0.6097
5	7161	80.58 <sup>5</sup>	0.5771
6	6359	84.77	0.5390 <sup>5</sup>
7	5610	89.15	0.5001
8	4843	94.59	0.4581
9	4087	102.08	0.4172
10	3688	108.02	0.3984
11	3280	117.36	0.3849
12	2973	129.44	0.3848
13	2816	141.18	0.3976

§ 4. *Comparison of the mixtures according to the law of corresponding states with carbon dioxide.* In Comm. N°. 59, Proc. Sept. 1900 methods are discussed for a graphical comparison of isothermals of mixtures with those of a simple substance. Here as well for carbon dioxide as for the two mixtures  $\log \frac{pv}{T}$ <sup>1)</sup> was drawn as a function of  $\log v$  for the different temperatures. (For the absolute zero we accepted — 273°.04 C.). If the law of corresponding states also holds for mixtures of normal substances it must be possible to

<sup>1)</sup> As the temperatures are so high that in the theoretical isothermals no negative pressures occur, the drawing of  $\log \frac{pv}{T}$  offers no difficulty.

make the corresponding isothermals of the different diagrams coincide by shifting them only in the direction of the  $\log v$ -axis.

I found that it was not possible to place the diagrams in such a way over each other that the isothermals of the whole system coincided; I, however, succeeded for the large volumes. According to KAMERLINGH ONNES this signifies that in the mixture the coefficients  $A, B, C, D, E, F$  of his series do not hang together with the coefficients of the pure substance at corresponding temperatures in such a manner as would follow from the law of corresponding states, but that for the volumes where the terms with  $D, E, F$  in comparison with the others are still so small that we may neglect the differences between these terms and those given by coefficients which would obey the law of corresponding states, the diagrams will coincide over such a large range of temperature that  $B$  and  $C$  may still be regarded as corresponding functions of temperature, hence a critical temperature and a critical pressure holding for this range of volume and temperature may be deduced from the law of corresponding states.

On the plate the diagrams are placed over each other so as to give the best agreement for the larger volumes. In the horizontal direction  $\log v$  is drawn, in the vertical  $\log \frac{pv}{T}$ . The complete lines refer to carbon dioxide, the dash lines to the first mixture, the dash-dots lines refer to the second mixture. The points for carbon dioxide are enclosed in circles, those for the first mixture in triangles, for the second in squares. The different isothermals are indicated by the letters  $a, b$ , etc., with which they are communicated in IV § 2 and V §§ 2 and 3. The points at the beginning and the end of the condensation are marked by  $b.c.$  and  $e.c.$ ; they are connected by curves which thus separate the homogeneous area from the area where separation occurs. Finally the plaitpoints and the points of contact are indicated by  $P$  and  $R$ ,  $K$  is the point adopted according to IV § 5 for the critical point of carbon dioxide.

It appears that the agreement for volumes larger than the critical is very satisfactory. In the smaller volumes, however, considerable systematic deviations from the law of corresponding states occur. We have already used these diagrams to determine the critical temperature, pressure and volume in the sense as explained above for the different mixtures. Although these results are satisfactory they will not be given here, as more accurate results may be expected from the same operations with diagrams projected on double the scale for the part concerned.

If on a  $pT$ -diagram we draw the point of contact- and the plait-

point curves, they are seen to touch each other at the end (critical point of pure carbon dioxide) in agreement with Comm. N<sup>o</sup>. 81 §§ 9 and 14 (Proc. Oct. 1902). In the investigated part the curves do not show the point of inflection found by VERSCHAFFELT with mixtures of hydrogen and carbon dioxide (Comm. N<sup>o</sup>. 47 Proc. Feb. 1899); they are always concave towards the  $T$ -axis.

**Physics.** — *“Isothermals of mixtures of oxygen and carbon dioxide.*

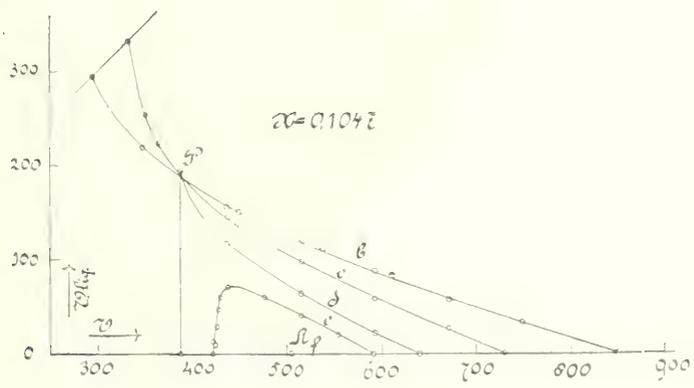
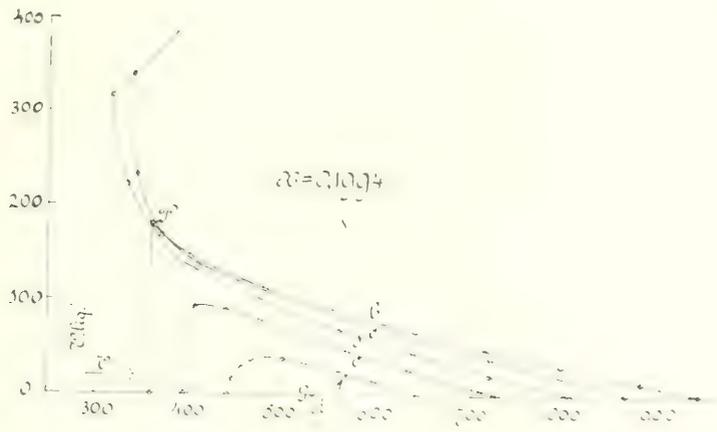
*V. Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide.”* By W. H. KEESOM. Communication N<sup>o</sup>. 88 (6<sup>th</sup> part) from the Physical Laboratory at Leiden, by Prof. KAMERLINGH ONNES.

(Communicated in the meeting of November 28. 1903).

§ 5. According to § 4 (p. 586) the observations allowed of a more accurate determination of the data for the critical point of the mixtures for the range of the larger volumes and the range of temperatures over which the observations have been made, in the sense as it has been explained there, than it was possible from the drawing given there. To this end diagrams were projected on double the scale for the points in the homogeneous area for which the volume is larger than 0.005; in these diagrams 0.0005 is represented by 1 mm. both for  $\log \frac{pv}{T}$  and for  $\log v$ . To determine the relation of the critical pressures independently and to test the relation of the critical temperatures of mixtures to that of pure carbon dioxide, diagrams were constructed for the same area, where  $\log \frac{pv}{T}$  is drawn as a function of  $\log p$ ; here 1 mm. represents: on the  $\log p$ -axis 0.00025, on the  $\log \frac{pv}{T}$ -axis 0.0005.

§ 6. The diagram for the mixture which had been transferred on tracing paper and in the middle of which a cross of axes was drawn in order to permit an accurate judgment of the agreement of the systems of axes for the two diagrams, was placed over the diagram for carbon dioxide, so that the  $\log v$ -, and  $\log p$ -axes respectively coincided, and then they were shifted until to the eye the isothermals of the mixture coincided with the system for carbon dioxide.

W. H. KEESOM. Isothermals of mixtures of oxygen and carbon dioxide. V. Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide.





Then we measured off for the isothermals of carbon dioxide which lay between those of the mixtures, the situation of the former with regard to the two neighbouring isothermals of the latter; this was done for a number of points distributed at regular distances. Let  $T_1$  and  $T_2$  be the temperatures of the two neighbouring isothermals of the mixture, and  $T'$  the temperature which for the mixture corresponds to that of the isothermal of carbon dioxide considered, then we obtain a great number of values for the relation  $\varphi = \frac{T' - T_1}{T_2 - T_1}$ .

We assumed that the isothermals coincided best when the mean square of the differences of  $\varphi$  and the mean  $\varphi$  were as small as possible.

Table XXIV, which refers to the comparison of the  $\log p$ -diagram of the mixture 0.1 with that of carbon dioxide shows in the 3<sup>d</sup> column the afore-mentioned mean square of the differences, viz. for the isothermals of 41.95° C. and 37.09° C. of carbon dioxide (after reduction to the same temperature interval  $T_2 - T_1$ ) combined, for the different superimposings of the coinciding systems indicated in the 1<sup>st</sup> column, while 1.85 of the mixture coincided with the values of  $\log p$  for carbon dioxide given in the 2<sup>d</sup> column.

T A B L E XXIV.

II	1.8850	0.012165
I	1.8840	0.010535
III	1.8829	0.004783
IV	1.8821	0.004440
V	1.8810 <sup>5</sup>	0.006221
Accepted: 1.88235		

In table XXV we find the data for the critical points of the mixtures thus found, combined with the data about the plaitpoints and the points of contact, and also the critical points of carbon dioxide and oxygen (the latter according to OLSZEWSKI).<sup>1)</sup>

<sup>1)</sup> It here appears that in the diagram given in § 4 (p. 587) in order to obtain the best agreement for the area of the larger volumes, the isothermals of the mixture 0.1 must be moved 5 mm. to the left, those of the second mixture 6 mm. to the right. The conclusions about the non-correspondence at the smaller volumes, however, still hold, the deviations even increase.

T A B L E XXV.

$x$	$T_{xpl}$	$T_{xr}$	$T_{xk}$	$p_{xpl}$	$p_{xr}$	$p_{xk}$	$v_{xpl}$	$v_{xr}$	$v_{xk}$
0	304.02	304.02	304.02	72.93	72.93	72.93			0.00443
0.1047	295.03	296.33	285.68	86.60	82.83	67.70	0.003878	0.005005	450
0.1994	285.55	289.31	272.92	99.65	89.20	67.30	3606	5322	431
1	154.2	154.2	154.2	50.7	50.7	50.7			

The values of  $T_{xk}$  derived from different diagrams and belonging to different coinciding isothermals, did not differ more than 0.5 deg.

We obtain for  $C_4 = \frac{T_{xk}}{T_0 p_{rk} v_{xk}}$  for the mixtures 0.1 and 0.2 respectively: 3.435 and 3.446, in sufficient harmony with the value 3.45, derived on p. 577 of this Comm. IV for carbon dioxide.

About the critical data the following may be remarked:  $v_{xk}$  shows a maximum in the range investigated; for  $x$  between 0.1 and 0.2  $p_{xk}$  descends much slower than between 0 and 0.1; the same holds in a less degree for  $T_{xk}$ .

§ 7. To calculate the quantities introduced in Comm. No. 75, (Proc. Dec. 1901):

$$\alpha = \frac{1}{T_k} \left( \frac{dT_{xk}}{dx} \right)_{x=0}, \quad \beta = \frac{1}{T_k} \left( \frac{dp_{xk}}{dx} \right)_{x=0}, \text{ etc.}$$

I have represented several quantities of Table XXV as functions of  $x$ . Observations for more values of  $x$  would be required to determine with some certainty how say  $v_{xk}$  depends on  $x$ . As it appeared that in consideration of the critical volume of oxygen, the data of table XXV, could not be satisfactorily represented by a quadratic function, I have added a term with  $x^3$  and have derived the coefficients from the data for carbon dioxide and oxygen (putting herefor  $C_4$  equal to the value for carbon dioxide) and the two mixtures. In this way I found:

$$\begin{aligned} T_{xk} &= T_k \{ 1 - 0.6563 x + 0.8350 x^2 - 0.6715 x^3 \}. \\ p_{xk} &= p_k \{ 1 - 1.0871 x + 4.1885 x^2 - 3.4063 x^3 \}. \\ v_{xk} &= v_k \{ 1 + 0.5422^5 x - 4.0310 x^2 + 3.2183^5 x^3 \}. \\ T_{xpl} &= T_k \{ 1 - 0.25792 x - 0.2349 x^2 \}. \\ p_{xpl} &= p_k \{ 1 + 1.6639 x + 1.5775 x^2 - 3.5462 x^3 \}. \\ T_{xr} &= T_k \{ 1 - 0.2474 x + 0.0898 x^2 - 0.3352 x^3 \}. \\ p_{xr} &= p_k \{ 1 + 1.4953 x - 1.9113 x^2 + 0.1112 x^3 \}. \end{aligned}$$

The data about  $T_{xpl}$  could be represented very accurately by a quadratic function.

We may expect that for values of  $x$  outside the range of observation these formulae will show important deviations from the experiment, because errors in the observations for  $x = 0.1$  and  $x = 0.2$  pass over increased into the values for the other range. This holds especially for  $T_{xk}$ ,  $p_{xk}$  and  $v_{xk}$ , which are exposed to so much more sources of errors than the other quantities.

§ 8. From the formulae given above we find:

$$\alpha = -0.6563 \quad , \quad \beta = -1.0871,$$

$$\gamma = \frac{1}{v_k} \left( \frac{dv_{xk}}{dx} \right)_{x=0}^1 = 0.5422^s,$$

while  $\alpha - \beta = 0.4308$ . That this value does not agree better with the value of  $\gamma$  found directly, while in § 6 we found that for the two mixtures the relation  $\frac{p_{xk} v_{xk}}{T_{xk}}$  was properly satisfied, is due to the representation by the above-mentioned functions, which may be expected to show just at the limits the largest deviations with regard to the differential quotients.

With a view to this the agreements between  $\frac{1}{T_k} \left( \frac{dT_{xpl}}{dx} \right)_{x=0}$  and  $\frac{1}{T_k} \left( \frac{dT_{xr}}{dx} \right)_{x=0}$  and between  $\frac{1}{p_k} \left( \frac{dp_{xpl}}{dx} \right)_{x=0}$  and  $\frac{1}{p_k} \left( \frac{dp_{xr}}{dx} \right)_{x=0}$  must be considered as satisfactory.

The values of  $\alpha$  and  $\beta$  derived from the values of  $\frac{1}{T_k} \left( \frac{dT_{xpl}}{dx} \right)_{x=0}$  and  $\frac{1}{p_k} \left( \frac{dp_{xpl}}{dx} \right)_{x=0}$  by means of the formulae (2a) and (2b) of Comm. No. 75 and the values found in this Comm. IV (p. 577) for the coefficients  $C_4$ ,  $\left( \frac{\partial \pi}{\partial \tau} \right)$  and  $C_4 \left( \frac{\partial^2 \pi}{\partial \omega \partial \tau} \right)$  occurring there, and the values of  $\alpha$  and  $\beta$  derived from  $\frac{1}{T_k} \left( \frac{dT_{xr}}{dx} \right)_{x=0}$  and  $\frac{1}{T_k} \left( \frac{dp_{xr}}{dx} \right)_{x=0}$  (as according to Comm. No. 81, Proc. Oct. 1902, p. 350 the same formulae hold for these quantities) have been combined with the values derived from the critical points  $K$  in Table XXVI, where the first column indicates from which point the data have been derived.

<sup>1)</sup> Comp. VERSCHAFFELT, Comm. N<sup>o</sup>. 81, Proc. Oct. 1902, p. 325.

T A B L E XXVI.

	$\alpha$	$\beta$
$K$	-0.6563	-1.0871
$P$	-0.6864	-1.2120
$R$	-0.6174	-0.9892

For this application of the formulae of Comm. N<sup>o</sup>. 75 it should be borne in mind that in the derivation of them we have used the law of corresponding states, while in § 4 (p. 587) it appeared that already at the critical volumes deviations could be detected. As long as  $x$ , however, is very small, the points  $P$  for the different mixtures will lie in an area where according to KAMERLINGH ONNES (comp. § 4) the law of corresponding states may be considered to hold at least to the first approximation, so that then we find an  $\alpha$  and a  $\beta$  for the critical points for that area. The same may be said of the points  $R$ . From the numbers given it appears that the values of  $\alpha$  and  $\beta$  with relation to those points, at least to the first approximation, agree with those relating to the critical point of the mixtures for the area of the larger volumes.

For the slopes on the  $pT$ -diagram for the plaitpoint- and the point of contact curve with small  $x$ , we find:

$$\frac{T_k \left( \frac{dp}{dT} \right)_{pl}}{\rho_k} = -6.451 \quad , \quad \frac{T_k \left( \frac{dp}{dT} \right)_r}{\rho_k} = -6.044,$$

values which agree sufficiently.

For the slopes of the curves which in the same diagram connect the points  $K$  and  $P$  we find:

$$\text{For the mixture 0.1: } \frac{p_{xpl} - p_{xk}}{T_{xpl} - T_{xk}} = 2.021$$

$$\text{For the mixture 0.2: } \quad \quad \quad 2.561.$$

For the curves which connect  $K$  and  $R$ :

$$\text{For the mixture 0.1: } \frac{p_{xr} - p_{rk}}{T_{xr} - T_{rk}} = 1.421$$

$$\text{For the mixture 0.2: } \quad \quad \quad 1.336.$$

From either side, therefore, there is an approach towards the value 1.610, which both quotients must have for very small  $x$ .

§ 9. From the formulae given in § 7 it would follow that the largest plaitpoint pressure to be expected in mixtures of carbon dioxide and oxygen would be 132 atms. (with  $x = 0.57$ ), while the largest value for  $T'_{xr} - T'_{xpl}$  would be expected to be 15.7 C. (with

$x = 0.63$ ). The last value will probably be too large, as the curves which, according to the afore-mentioned formulae, represent  $T_{xr}$  and  $T_{xpl}$  as a function of  $x$ , and which for  $x = 0$  almost touch each other, do not do so for  $x = 1$  and hence for larger  $x$  yield too large values for  $T_{xr} - T_{xpl}$ .

§ 10. *Purity of the carbon dioxide.* The values of  $a$  and  $\beta$  found and the increase of vapour pressure found at  $25^{\circ}.55$  C. with the condensation: 0.07 atm. (comp. this Comm. IV, p. 567) allow us to judge of the purity of the carbon dioxide used. By means of formula (9) of Comm. N<sup>o</sup>. 79, Proc. April '02, which for the unities used in this paper may be written

$$(v_2 - v_1) (p_1 - p_2) = A_t x (e^k + e^{-k} - 2)$$

if

$$A_t = 1 + 0.0036625 t$$

and

$$k = \left\{ \alpha \frac{T dp}{p dT} - \beta \right\} \frac{p (v_2 - v_1)}{A_t}$$

we find, on the supposition that the admixture were oxygen, and using for  $a$  and  $\beta$  the values derived from the point  $K$ :

$$x = 0.00027.$$

§ 11. *Retrograde condensation.* In the annexed plate we give for the two mixtures investigated curves which represent  $v_{liq}$  as function of  $v$  according to the tables given in sections 2 and 3 (p. 579 ff.). The curves for the different temperatures are marked by the letters, by which the corresponding isothermals have been indicated. The numbers on the plate hold for the unity 0.00001.

**Physics.** — "*Isothermals of mixtures of oxygen and carbon dioxide.*"

VI. *Influence of gravitation on the phenomena in the neighbourhood of the plaitpoint for binary mixtures.* By W. H. KEESOM. Communication N<sup>o</sup>. 88 (7<sup>th</sup> part) from the Physical Laboratory at Leiden, by Prof. KAMERLINGH ONNES.

(Communicated in the meeting of November 28, 1903).

§ 1. In this Communication V, § 1 (p. 577) it was remarked that the liquid meniscus at the end of the condensation over a certain range of temperatures appeared or disappeared in the tube. KUENEN (Comm. N<sup>o</sup>. 17, Zittingsversl. May 1895) was the first who explained these phenomena by the theory of VAN DER WAALS on the influence of gravitation on the thermodynamic equilibrium in mixtures. (Contin. II

p. 30). The following pages may show that there is also a quantitative agreement between the phenomena and that theory.

§ 2. In the mixture with the molecular proportion 0.1047 of oxygen the meniscus by increasing the volume at 21°.86 C. appeared at the top of the tube, at 21°.94 C. it was formed at the mark 44.99 (stirrer below, mercury meniscus at 41.66); at 22°.17 C. the meniscus appeared at the bottom of the tube, at 22°.09<sup>s</sup> C. it was formed at the mark 43.93 (stirrer below, mercury meniscus at 41.57). The top of the tube was at the mark 47.40 (cm).

In the mixture of the molecular proportion 0.1994 the meniscus appeared at 13°.12 C. at the bottom of the tube, at 13°.07 C. it appeared at the mark 38.5 (stirrer above, mercury meniscus at 37.4); at 11°.89 C. the meniscus appeared at the top of the tube, at 11°.92 C. it appeared at 42.3 (stirrer below, mercury meniscus at 37.7). The top of the tube was at the mark 42.97. We may assume that for this mixture the limits between which the meniscus appears in the tube are: 13°.10 C. and 11°.90 C.

In these observations the volume from the homogeneous state was increased by small variations; in this case the meniscus even without stirring appears quickly at its definite place, which is not altered by stirring. If on the contrary we start from the state where separation into two phases occurs and the volume is decreased, the meniscus only disappears after stirring and then suddenly; hence it seems that in the former case the equilibrium is established much sooner<sup>1)</sup>.

§ 3. In order to be able to compare the observations discussed above with theory, I have found what may be deduced for it if  $x$  is supposed very small. It may be easily derived from considerations of VAN DER WAALS (Contin. II, p. 30 ff.) that the phases which are in equilibrium are determined by the following pair of equations:

$$\begin{aligned} F dv &= \left\{ \frac{M_1(1-x) + M_2x}{v} \left( \frac{\partial^2 \psi}{\partial v^2} \right) + (M_2 - M_1) \left( \frac{\partial^2 \psi}{\partial v \partial x} \right) \right\} gdh \\ F dx &= - \left\{ \frac{M_1(1-x) + M_2x}{v} \left( \frac{\partial^2 \psi}{\partial v \partial x} \right) + (M_2 - M_1) \left( \frac{\partial^2 \psi}{\partial v^2} \right) \right\} gdh \end{aligned} \quad \dots (1)$$

Here  $\psi$  is the free energy for the molecular quantity of the mixture,  $v$  the molecular volume in cc.,  $M_2$  the molecular weight of the substance of which the quantity in the mixture is indicated by  $x$

<sup>1)</sup> Compare with this what has been remarked in this Comm IV p. 574 about the circumstance that the equilibrium was not immediately reached after the heating of carbon dioxide at the critical point. Comp. also GOUY, C. R. t. 116, p. 1291 and MATHIAS, Le Point critique des corps purs, p. 89.

(admixture),  $M_1$  that of the other substance, while

$$F = \left( \frac{\partial^2 \Psi}{\partial r^2} \right) \left( \frac{\partial^2 \Psi}{\partial v^2} \right) - \left( \frac{\partial^2 \Psi}{\partial r \partial v} \right)^2.$$

The equations (1) determine on the  $\Psi$ -surface a curve which according to KUENEN (l. c. p. 6) I call the gravitation-curve<sup>1)</sup>.

From (1) we derive:

$$\frac{dv}{dx_{gr}} = \left( \frac{\partial v}{\partial x} \right)_{\rho T} - \frac{F'}{\left( \frac{\partial^2 \Psi}{\partial v^2} \right)} \cdot \frac{\frac{M_1(1-v) + M_2 v}{v}}{\frac{M_1(1-v) + M_2 v}{v} \left( \frac{\partial^2 \Psi}{\partial v \partial r} \right) + (M_2 - M_1) \left( \frac{\partial^2 \Psi}{\partial r^2} \right)}.$$

From this equation it follows that at the plaitpoint  $\frac{dv}{dx_{gr}} = \left( \frac{\partial v}{\partial x} \right)_{\rho T}$ , hence the gravitation-curve touches the isobar, and accordingly also the spinodal curve, for which  $F' = 0$ . Then also at the following point of the gravitation-curve which passes through the plaitpoint, to the first approximation  $\frac{dv}{dx_{gr}} = \left( \frac{\partial v}{\partial x} \right)_{\rho T}$ , or at the plaitpoint

$$\frac{d^2 v}{dx_{gr}^2} = \left( \frac{\partial^2 v}{\partial x^2} \right)_{\rho T}.$$

By means of this we have for a point of the gravitation curve which passes through the plaitpoint, in the neighbourhood of the latter:

$$F = \frac{1}{2} (x - x_{Tpl})^2 \left\{ \left( \frac{\partial F}{\partial r} \right) \left( \frac{\partial^2 r}{\partial x^2} \right)_{\rho T} + \left( \frac{\partial^2 F}{\partial r^2} \right) \left( \frac{\partial r}{\partial x} \right)_{\rho T}^2 + 2 \left( \frac{\partial^2 F}{\partial r \partial v} \right) \left( \frac{\partial r}{\partial x} \right)_{\rho T} + \left( \frac{\partial^2 F}{\partial v^2} \right) \right\},$$

in which equation the differential quotients of  $F$  and  $v$  must be taken at the plaitpoint. If here we put  $x_{Tpl}$  small, we may reduce this form using reductions as in Comm. N<sup>o</sup>. 75, § 7 (Proc. Dec. 1901), to the first approximation to:

$$F = -\frac{1}{2} (x - x_{Tpl})^2 \frac{(M_1 R T_k)^3}{x^3 T_{pl}} \frac{\left( \frac{\partial^2 p}{\partial v^3} \right)_T}{\left( \frac{\partial p}{\partial x} \right)_{vT}}.$$

in which relation the differential quotients of  $p$  must be taken at the critical point of the simple substance.

<sup>1)</sup> Comp. also KUENEN, l. c. Fig. 2.

<sup>2)</sup> This has been demonstrated for the gravitation-curve on the  $\Psi$ -surface for a constant mass in a different manner by KUENEN, l. c. p. 8.

If also in the second member of the equations (1) we put  $x$  small we may integrate the latter to

$$\frac{1}{3} (x - x_{T_{pl}})^3 = -2 \frac{x^3 T_{pl}}{(M_1 R T_k)^3} \frac{\left(\frac{\partial p}{\partial v}\right)_{vT} M_1}{\left(\frac{\partial^2 p}{\partial v^2}\right)_T} g h + \text{constant} . . \quad (2)$$

From this equation we may easily derive the value of  $x_{T_{pl}}$  if the mean composition  $X$ , the height of the tube  $H$  and the place where the meniscus appears are given, and hence also  $x_{T_{pl}} - X$ , if this takes place just at the top or at the bottom of the tube. Let  $T'_{X_{pl}}$  be the plaitpoint temperature belonging to the composition  $X$ ,  $T_{b_{pl}}$  the temperature at which the meniscus appears just at the top of the tube,  $T_{o_{pl}}$  the same for the bottom of the tube, then we obtain :

$$T_{b_{pl}} - T'_{X_{pl}} = -\frac{3}{4} \frac{X}{M_1 R T_k} \left(\frac{\partial p}{\partial v}\right)_{vT} \sqrt[3]{\frac{M_1 g H}{v_k \left(\frac{\partial^3 p}{\partial v^3}\right)_T}} \cdot \frac{dT'_{X_{pl}}}{dx},$$

and for  $T'_{o_{pl}}$  the same formula with the other sign.

If as in Comm. N<sup>o</sup>. 75, § 2 we introduce the law of corresponding states this formula becomes :

$$T_{b_{pl}} - T'_{X_{pl}} = -\frac{3}{4} X \left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right) \right\} \cdot \frac{dT'_{X_{pl}}}{dx} \sqrt[3]{\frac{M_1 g H}{p_k v_k \cdot C_4^3 \left(\frac{\partial^3 \pi}{\partial \omega^3}\right)}}, \quad (3)$$

where for  $\frac{dT'_{X_{pl}}}{dx}$  we still could substitute the form given in Comm. N<sup>o</sup>. 75 equation 2a.

§ 4. In the comparison of formula (3) with the observations mentioned in § 2 I have assumed that for the area of the plaitpoints the law of corresponding states holds to the first approximation, and I have taken for  $\alpha$  and  $\beta$  the values derived from the observations of the plaitpoints (comp. this Comm. V, § 8).

For  $\left(\frac{\partial^3 \pi}{\partial \omega^3}\right)$  I have taken the value  $-5.3$  calculated by VERSCHAFFELT (Comm. Suppl. N<sup>o</sup>. 6, Proc. June 1903, p. 121) from the series of KAMERLINGH ONNES, which value with  $C_4 = 3.45^1$ ) gives  $C_4^3 \left(\frac{\partial^3 \pi}{\partial \omega^3}\right) = -218^2)$ .

With the value  $H = 5.8$  cm., and the critical density for carbon dioxide

<sup>1)</sup> Comp. this Comm. IV, p. 577.

<sup>2)</sup> Comp. Comm. N<sup>o</sup>. 75, Proc. Dec. 1901, p. 307.

$\frac{M_1}{v_k} = 0.443$ , derived from the data of this Comm. IV, we find, supposing that formula (3) were to hold as far as the value  $x = 0.1047$ :

$$T_{b,pl} - T_{o,pl} = 0.23^\circ.$$

The agreement with the value found in § 2 (between  $0^\circ.15$  C. and  $0^\circ.31$  C.) is better than might be reasonably expected with the suppositions made. The circumstance that for the second mixture  $1^\circ.20$  C. was found for this shows that for this value of  $x$  terms with  $x^2$  etc. have already a preponderating influence.

**Physics.** — "*Hysteretic orientatic-phenomena.*" By Prof. H. E. J. G. DU BOIS. (Communicated by Prof J. D. VAN DER WAALS).

(This paper will not be published in these Proceedings).



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday February 27, 1904.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 27 Februari 1904, Dl. XII).

C O N T E N T S.

H. W. BAKHUIS ROOZEBOOM and A. H. W. ATEN: "The melting point lines of the system sulphur + chlorine", p. 599.

A. W. VISSER: "Enzymactions considered as equilibria in a homogenous system". (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 605.

A. J. P. VAN DEN BROEK: "The foetal membranes and the placenta of *Phoca vitulina*." (Communicated by Prof. L. BOLK), p. 610.

W. KAPTEIJN: "On the differential equation of MONGE", p. 620.

W. A. VERSLUYS: "The singularities of the focal curve of a plane general curve touching the line at infinity  $\tau$  times and passing  $\varepsilon$  times through each of the imaginary circle points at infinity." (Communicated by Prof. P. H. SCHOUTE), p. 621.

W. A. VERSLUYS: "On the position of the three points which a twisted curve has in common with its osculating plane." (Communicated by Prof. P. H. SCHOUTE), p. 622.

A. SMITS: "A contribution to the knowledge of the course of the decrease of the vapour tension for aqueous solutions." (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 628. (With one plate).

H. KAMERLINGH ONNES and C. A. CROMMELIN: "On the measurement of very low temperatures. VI. Improvements of the protected thermoelements; a battery of standard-thermoelements and its use for thermoelectric determinations of temperature", p. 642. (With 2 plates).

J. E. VERSCHAFFELT: "Contributions to the knowledge of VAN DER WAALS'  $\psi$ -surface. VIII. The  $\psi$ -surface in the neighbourhood of a binary mixture which behaves as a pure substance." (Communicated by Prof. H. KAMERLINGH ONNES), p. 649. (With one plate).

The following papers were read:

**Chemistry.** — "*The melting point lines of the system sulphur + chlorine.*" By Prof. H. W. BAKHUIS ROOZEBOOM and A. H. W. ATEN.

(Communicated in the meeting of January 30, 1904).

The boiling point lines of this system have already been described at the meeting in May 1903. These led to the view that the compound  $S_2Cl_2$  in the liquid and vaporous condition is but very little dissociated and also that further compounds occur at a not too low temperature in liquids with a higher proportion of chlorine.

A closer study of the changes in volume which take place in these liquids and of the velocity with which this happens has rendered it probable that  $\text{SCl}_2$  is chiefly formed and in addition also  $\text{SCl}_4$ .

The equilibrium between  $\text{S}_2\text{Cl}_2$ ,  $\text{SCl}_2$ ,  $\text{SCl}_4$  and  $\text{Cl}_2$  which takes place in the liquids is not modified to any extent by cooling below  $0^\circ$  and remains totally unchanged at those low temperatures at which these mixtures may deposit solid substances. This gives rise, during the solidification, to very peculiar phenomena which, up to the present, have not been noticed with other systems but which may be explained by the views of the phase doctrine.

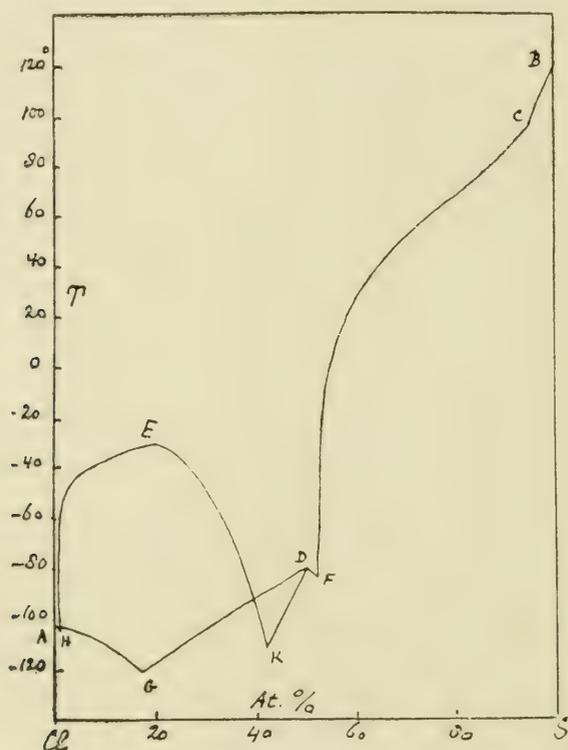


Fig. 1.

On the other hand nothing noteworthy occurs with mixtures containing 50—100 atomic per cent of S. These behave entirely like mixtures  $\text{S}_2\text{Cl}_2 + \text{S}$ . The melting point of  $\text{S}_2\text{Cl}_2$  ( $-80^\circ$ ) is lowered by sulphur to F; the melting point of sulphur is also lowered by  $\text{S}_2\text{Cl}_2$  from B ( $120^\circ$ ) to F.

At a low temperature the solubility of S in  $\text{S}_2\text{Cl}_2$  is very small. The solubility or melting point line of S consists of two curved lines

FC and CB, which at  $C=96^\circ$  join at an angle. The top line relates to monoclinic, the lower one to rhombic sulphur.

Mixtures of 0—50 atomic % sulphur may on cooling, give as solid phases  $Cl_2$ ,  $S_2Cl_2$  and  $SCl_4$ .

The manner in which they are successively deposited may be best explained by first observing in what manner the solidification of a mixture of these three substances would take place when the  $SCl_4$  could be considered as an independent third component.

This would be the case if this compound did *not* dissociate in the liquid condition and also was not formed from liquid  $S_2Cl_2$  and  $Cl_2$ . The system would then behave as a ternary system, the solidification phenomena of which could only be completely represented by a spacial figure.

We may also, however, disregard the constitution of the liquid and express its gross composition only in  $Cl_2$  and  $S_2Cl_2$  which is all the more justifiable as there is no means of determining the amount of  $SCl_4$  in the presence of  $Cl_2$  and  $S_2Cl_2$ .

We then obtain a representation in a plane (see fig. 2) which is the projection of the spacial figure<sup>1)</sup>.

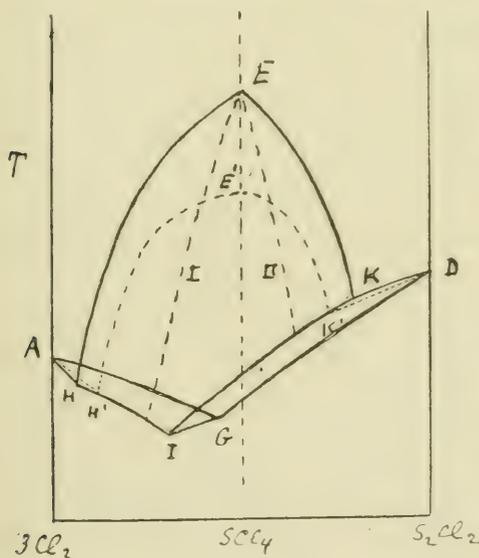


Fig. 2.

In this figure EH and HA are the solidification lines of the binary mixtures  $SCl_4$  and  $Cl_2$ , EK and KD those of  $SCl_4$  and  $S_2Cl_2$ , AG and DG those of  $Cl_2$  and  $S_2Cl_2$ .

The ternary mixtures whose compositions lie within the region IHAG first deposit solid chlorine, those in IKDG solid  $S_2Cl_2$  and those in HEKI solid  $SCl_4$ . For each gross composition there exists a greater or smaller series of molecular arrangements which cannot be represented in the plane, but on which the temperature at which the one or other solid phase

commences to be deposited depends. (Some mixtures may even separate more than one phase according to their molecular composition).

<sup>1)</sup> We must then accept as components:  $3 Cl_2$  and  $S_2Cl_2$  in order that the middle of the abscissa axis represents the composition  $SCl_4$ .

This difference is further shown by the different crystallisation paths which on further cooling are traversed by mixtures of the same gross composition.

These crystallisation paths start in each of the regions mentioned from the point representing the melting point of the solid phase, that is from A, D and E respectively, and indicate the series of mother liquors which remain, during a continued cooling, at each temperature. The crystallisation paths in the first region end in HI or IG, those for the second in KI or IG, for the third in HI or KI. The lines I and II schematically indicate two similar paths in the last region, the vertical line EE' is a third one which applies to a liquid of the gross composition  $\text{SCl}_4$ .

As soon as the crystallisation paths arrive at HI, KI or GI, the subsequent solidification takes place along these lines, each time with deposition of two solid phases:  $\text{Cl}_2 + \text{SCl}_4$  on HI,  $\text{S}_2\text{Cl}_2 + \text{SCl}_4$  on KI and  $\text{Cl}_2 + \text{S}_2\text{Cl}_2$  on GI.

Finally the last liquid solidifies in I to a ternary eutecticum of the three phases.

This would be the state of affairs if — as has been said —  $\text{SCl}_4$ ,  $\text{S}_2\text{Cl}_2$  and  $\text{Cl}_2$  were miscible in all proportions without transformation.

If, however,  $\text{SCl}_4$  were a dissociable compound whose formation and decomposition led to complete equilibria at all solidification temperatures, then instead of the solidification described another would occur along the lines AH', H'E'K', K'D causing the system to appear as a binary one in which occurs a compound which enters into equilibrium with its components in the liquid condition. The position of these lines within the figure of the ternary system is determined by the degree of dissociation of the liquid compound. If this is extremely small, these lines approach to AH, HEK and KD, if very large they approximate to AG and GD and the compound does not appear as a solid phase. Solid  $\text{Cl}_2$  is deposited along AH', solid  $\text{SCl}_4$  along H'E'K', solid  $\text{S}_2\text{Cl}_2$  along K'D; H' and K' are two eutectic points where complete solidification takes place. These three lines are not only the first series of solidifying points of the different mixtures, but at the same time the crystallisation paths of all mixtures.

Now with mixtures of  $\text{S}_2\text{Cl}_2$  and  $\text{Cl}_2$  neither the first nor the second case is quite realised. At the low temperatures at which the solidifications take place,  $\text{Cl}_2$ ,  $\text{S}_2\text{Cl}_2$  and  $\text{SCl}_4$  behave as independent components; for instance  $\text{Cl}_2$  and  $\text{S}_2\text{Cl}_2$  may be mixed in the liquid condition without entering into combination and in this way the two solidifying lines AG and GD (fig. 1 and 2) of these mixtures

have been determined. Neither does  $\text{SCl}_4$  undergo decomposition at those low temperatures. If, therefore, it were possible to isolate pure  $\text{SCl}_4$ , all imaginable mixtures thereof with  $\text{Cl}_2$  and  $\text{S}_2\text{Cl}_2$  or with both might be obtained and the further portions of fig. 2 could then be constructed. This, however, is not the case.

On account of the extreme minuteness of its crystals and the low temperature at which crystallisation takes place, the compound  $\text{SCl}_4$  cannot be isolated in a pure condition and cannot, therefore, be added in definite proportions to  $\text{Cl}_2$  or  $\text{S}_2\text{Cl}_2$ . By exposing various mixtures of these compounds to temperatures of  $0^\circ$  and higher it is possible to cause the voluntary formation of those quantities of  $\text{SCl}_4$  which are in equilibrium with  $\text{Cl}_2$  and  $\text{S}_2\text{Cl}_2$  at the temperature chosen. As these do not change much with the temperature, the same series of mixtures is fairly well retained on cooling to the crystallisation temperatures. The number of ternary mixtures whose crystallisation may be investigated is, therefore, restricted to one for each gross composition.

We, therefore, always obtain for the first solidifying points a series such as  $\text{AH'E'K'D}$  in fig. 2, just as if we were dealing with a binary mixture in which a dissociable compound occurred. If, however, the equilibrium in the liquid does not change when  $\text{Cl}_2$ ,  $\text{SCl}_4$  or  $\text{S}_2\text{Cl}_2$  crystallises out, the system on solidification must behave as a ternary one.

This should have appeared in practice by the fact that the curve of the first solidifying points did not also represent the path of crystallisation, and, therefore, the mother liquor left after cooling each mixture to a lower temperature differed in composition from that given by the point on the curve corresponding with the temperature in question. Owing to the nature of the crystals, however, it was impossible to remove the mother-liquor with a pipette.

It was, however, possible to prove in the case of a liquid of the gross composition  $\text{SCl}_4$  that this does not completely solidify to  $\text{SCl}_4$  at  $\text{E}'$ , but only commences to deposit  $\text{SCl}_4$  at that temperature ( $-30^\circ$ ), which quantity increases on further cooling, but in such a manner that no complete solidification takes place below  $-80^\circ$ . In the points on both sides of  $\text{E}'$  the continuity is still more pronounced and this makes the accurate determination of even the first solidifying points very difficult.

In the second place the solidification of the different mixtures ought not to be complete in  $\text{H}'$  or in  $\text{K}'$ , but only in  $\text{I}$  after traversing the crystallisation paths  $\text{H'I}$  and  $\text{K'I}$ .

This is confirmed qualitatively but the exact determination of the lines HI and KI and consequently also of the ternary eutecticum proved to be impossible.

In this way no more was obtained than is indicated in Fig. 1, namely the solidification lines AG and GD for the mixtures of  $\text{Cl}_2$  and  $\text{S}_2\text{Cl}_2$  in which no compound had formed and besides these the series of the first solidifying points AH, HEK and KD for the partially combined liquids formed at  $0^\circ$ .

These lines therefore correspond with the accentuated lines in Fig. 2. The true melting point of  $\text{SCl}_4$ , without decomposition of the liquid (E Fig. 2) is therefore not yet known. If  $\text{SCl}_4$  could have been prepared in pure crystals, this might have probably been determined as it would presumably be situated below the temperature where the liquid compound shows perceptible decomposition.

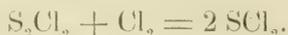
This is rendered more probable by the observation that notwithstanding their minuteness the crystals of  $\text{SCl}_4$  when rapidly heated, are quite permanent up to  $-20^\circ$ .

Fig. 1 does not agree with fig. 2 in an important point. In the latter DK is placed above DG, in the first DK is found below DG. DG represents the lowering of the melting point of  $\text{S}_2\text{Cl}_2$  by added  $\text{Cl}_2$  when this remains unchanged: DK when a portion of it combines with a part of the  $\text{S}_2\text{Cl}_2$  to  $\text{SCl}_4$  according to the equation



If we now compare the total amount of the foreign molecules which occur along with the  $\text{S}_2\text{Cl}_2$ , for the same total amount of  $\text{Cl}_2$ , these numbers are smaller in the case of a partial formation of  $\text{SCl}_4$  than when this is not the case. According to this supposition DK ought to be situated higher than DG.

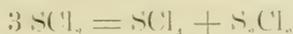
As in practice, the reverse position was found we must look for a cause which may explain this fact. We find this by supposing that besides  $\text{SCl}_4$  there is also formed in the liquid a considerable proportion of  $\text{SCl}_2$  according to the equation



By taking this view the number of foreign molecules mixed with the  $\text{S}_2\text{Cl}_2$  becomes greater owing to the formation of  $\text{SCl}_2$  than without this.

The formation in the liquid of an amount of  $\text{SCl}_2$  exceeding that of  $\text{SCl}_4$  which had already become probable by the dilatometric experiments has, therefore, been confirmed. The slow crystallisation of  $\text{SCl}_4$  will now be better understood; but the liquids between  $\text{Cl}_2$  and  $\text{S}_2\text{Cl}_2$  should now be considered not as ternary but as quater-

nary mixtures. If during the crystallisation  $\text{SCl}_2$  in the solution does not yield  $\text{SCl}_4$  according to the equation



solid  $\text{SCl}_2$  ought to be found somewhere on the way to complete solidification. This point could not be decided.

**Chemistry.** — “*Enzymactions considered as equilibria in a homogeneous system.*” By A. W. VISSER. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of January 30, 1904.)

1. A number of facts exist which indicate that the reactions created by enzymes are reversible. CROFT-HILL<sup>1)</sup> succeeded in partly converting a concentrated solution of glucose into a disaccharide with the aid of maltase and reversibly the disaccharide into glucose. He supposed it to be maltose but afterwards EMMERLING<sup>2)</sup> proved it to be isomaltose; the fact however remains that maltase may cause a reversible formation of polysaccharides. Recently, CROFT-HILL<sup>3)</sup> has further proved that there is formed from glucose by means of maltase a new crystallised biglucose called revertose, he thinks it probable that also maltose may be formed<sup>4)</sup>. KASTLE and LOEWENHART<sup>5)</sup> and afterwards HANRIOT<sup>6)</sup> found that the fat-splitting enzyme lipase is capable of resolving butyricester into butyric acid and alcohol and on the other hand of forming the ester from the decomposition products. EMMERLING<sup>7)</sup> noticed the regeneration of amygdalin from nitrilglucoside-amygdalate and glucose under the influence of maltase. E. FISCHER and FRANKLAND ARMSTRONG<sup>8)</sup> prepared with the aid of Kefir-lactase a disaccharide from a mixture of galactose and glucose called isolactose, which up to the present could not be isolated in a state of purity. The same authors also found that kefir-lactase forms a disaccharide from glucose alone and that emulsin does the same from a mixture of glucose and galactose.

<sup>1)</sup> J. C. S. **73**, 634 (1898).

<sup>2)</sup> Ber. **34**, 600, 2206 (1901).

<sup>3)</sup> J. C. S. **83**, 578 (1903).

<sup>4)</sup> All these experiments show that the substance supposed to be maltase still contains other ferments.

<sup>5)</sup> Am. Ch. J. **26**, 533 (1901).

<sup>6)</sup> C. R. **132**, 212 (1901).

<sup>7)</sup> Ber. **34**, 3810 (1901).

<sup>8)</sup> Ber. **35**, 3151 (1902).

From several experiments I have made, I think the conclusion may be drawn that it is probable that saccharose may be regenerated to a slight extent from glucose and fructose by means of invertase, whilst it may be taken as proved with tolerable certainty that salicin may be regenerated from saligenin and glucose by means of emulsin.

If, with the usual precautions, a  $N/4$  solution of saccharose<sup>1)</sup> is exposed to the action of invertase, the former is resolved into glucose + fructose and the liquid shows a final polarisation of  $-3^{\circ}.26$ °).

If a similar solution is inverted by  $N/4$  HCl the final polarisation becomes  $-3^{\circ}.42$ .

A solution containing the same amount of glucose and fructose<sup>3)</sup> as is formed after total inversion of a  $N/4$  solution of saccharose also gives a final polarisation of  $-3^{\circ}.42$ .

A solution containing equal quantities of glucose + fructose and which showed at the start a polarisation of  $-12^{\circ}.46$  gave after two months action of invertase a polarisation of  $-12^{\circ}.29$ . These experiments have been repeated a few times.

A  $N/16$  solution of salicin, resolved by emulsin into saligenin and glucose, gave a final polarisation of  $1^{\circ}.03$  whilst a solution containing as much saligenin and glucose as ought to be formed by the complete decomposition of a  $N/16$  solution of salicin shows a polarisation of  $1^{\circ}.18$ . Such a solution which contains the same amount of emulsin as the  $N/16$  solution of salicin gave after a month a polarisation of  $1^{\circ}.03$ .

The formation of salicin, which shows that the reaction is reversible, may be proved qualitatively in the following manner. The glucose was got rid of as much as possible by fermentation and after filtering, the saligenin was completely removed by agitating the solution with ether. The liquid was now concentrated to about 5 c.c. on the waterbath. To one half of it was added a drop of ferricchloride solution (1:10); this gave no coloration showing the absence of saligenin, a mere trace of which would give a blue coloration. The remainder was evaporated to dryness and gave with  $H_2SO_4$  a red coloration (formation of rutilin). 0.5 c.c. of a 1 %

1) All solutions mentioned contained 0.5 % of sodium fluoride to prevent bacterial action: all apparatus and utensils were also previously sterilised.

2) A Lippich-polarimeter was used. The readings were accurate up to  $0^{\circ}.02$  and all observations were made at  $25^{\circ}$ .

3) I have to thank Mr. ALBERDA VAN EKENSTEIN for supplying me with these perfectly pure sugars.

salicin solution and 1 gram of glucose was diluted with a 1% saligenin solution up to 50 c.c.; the 0.005 gram of salicin present could be detected in the manner described. Great care must be taken to ensure the complete removal of the saligenin, as this also gives a red coloration with strong  $H_2SO_4$ .

I think these experiments warrant the conclusion that the resolution of saccharose by invertase may be probably considered as an equilibrium reaction and that this is tolerably certain in the case of the action of emulsin on salicin.

As regards the last reaction, TAMMANN had come to the conclusion that, although incomplete, it is not however a limited reaction, as the limit did not undergo retrogression on adding the products of decomposition. TAMMANN however has not worked with sterile solutions so that, as others have already observed, his experiments are not conclusive. Moreover, the figures found by TAMMANN for the concentration in the condition of equilibrium at 0° and 25° differ not inconsiderably from my own.

2. Dynamical researches as to the action of enzymes have soon shown that certain decompositions do not proceed in such a simple manner as in the case where acids are employed. Although O'SULLIVAN and TOMPSON first believed that the hydrolytic resolution of saccharose by invertase is represented by the same simple formula (for reactions of the first order) as that for the same reaction by H-ions, TAMMANN and DUCLAUX have demonstrated that such is by no means the case. This has been confirmed by subsequent researches particularly by those of HENRI. The reaction coefficient of the system saccharose + invertase calculated according to the logarithmic formula appeared to increase; for the system salicin + emulsin it appeared to decrease with the time. So TAMMANN comes to the conclusion that the enzymes do not conform to the same laws as the inorganic catalyzers and that these laws will not readily be traced, and DUCLAUX is of opinion that the laws of physical chemistry do not apply at all to enzym actions.

As the dynamic investigation of the action of ferments had only just commenced, these conclusions could hardly be accepted as final. The exhaustive researches published in 1901 by VICTOR HENRI <sup>1)</sup> and afterwards continued <sup>2)</sup> have indeed proved that the course of ferment actions may decidedly be expressed by a formula. It has already been observed that the resolution of saccharose by invertase proceeds more rapidly than is expressed by the formula for reactions

<sup>1)</sup> Z. phys. ch. 39, 194 (1901).

<sup>2)</sup> Lois générales de l'action des diastases. Thèses, Paris, Février 1903.

of the first order: it was therefore obvious to assume here an accelerating autocatalysis, a reaction for which OSTWALD<sup>1)</sup> had worked out a formula. HENRI has now followed this course indicated by OSTWALD and deduced an empirical formula which, when applied to his experiments led to coefficients which may be taken as practically constant for N/100 to N solutions. HENRI accepted a theory of the mechanism of the action of invertase according to which the ferment should enter into combination with saccharose as well as with fructose (according to an equilibrium-reaction). By now trying different values for the equilibrium constants of these two reactions, he arrives at two figures, the introduction of which into the formula leads to the said constants. I believe to have succeeded in proving that HENRI'S views are not correct judging from his own experimental data and from my own observations.

Recently HERZOG<sup>2)</sup>, for the resolution of salicin by emulsin, (where on applying the formula for reactions of the first order the coefficients regularly decrease) has applied OSTWALD'S formula for reactions with negative autocatalysis<sup>3)</sup> to HENRI'S and TAMMANN'S experiments on the said reaction; he has found that this formula leads to reaction coefficients which may be considered as constants. These constants change with the initial concentration of the salicin solutions.

HERZOG however observes that OSTWALD'S differential equation for negative autocatalytic transformations is incomplete "and that it would be better to give it the form of a reaction of a higher order". This was already done by me some time ago.

3. Given the fact (now tolerably well substantiated) that enzymatic actions are equilibrium reactions, I have taken a view of the theory of these decompositions different from that hitherto accepted and first deduced formulae giving the relation between velocity of reaction and chemical equilibrium. These formulae differ from those at present applied to this case<sup>4)</sup>; I have deduced them for mono-, bi- and trimolecular equilibrium reactions<sup>5)</sup>, first tested them in well-known cases (ester formation; the transformation studied by KÜSTER<sup>6)</sup> etc) also by SCHOORL'S observations on the action of sugars on urea<sup>6)</sup> which I have myself extended and subsequently applied them to the observations of HENRI as well as to my own series of determinations relating to the saccharose and salicin resolutions. The results of this

1) Lehrbuch, II, 2, 262.

2) These Proc. VI November 28 1903, p. 332.

3) Lehrbuch II, 2, 270.

4) OSTWALD'S Lehrbuch II, 2, 251, e.v.

5) Z. phys. ch. 18, 161 (1895).

6) Rec. 22, 31, Dissertation, 1902.

application are very satisfactory. I have further been able to develop for the activity of the enzymes an intensity formula wherein, besides the concentrations of the solutions, the constants found experimentally occur and which I believe, gives a fair representation of the quantitative progress of the enzym actions as studied by previous observers and myself.

4. These mathematical deductions and the details of the other results obtained by me will be published fully elsewhere. I may only remark further, that my results show that, starting with a  $N/2$  saccharose solution (171 grams per litre) we arrive at a final condition where fully 1 gram of saccharose still remains present. The inversion therefore proceeds to an amount greater than 99  $\%$ . This seems also the case in the resolution of salicin.

My experiments further show :

1<sup>st</sup>. that the two ferments invertase and emulsin retain their quantitative activity for some weeks in properly sterilised solutions.

2<sup>nd</sup>. that the average factor for the change of the velocity of the saccharose decomposition with the temperature equals 2 for 10° between 0° and 25°.

3<sup>rd</sup>. that by a change of temperature from 0° to 25° the equilibrium is displaced very little or not at all, which quite agrees with theory as the caloric effect of the reaction is very small.

4<sup>th</sup>. that at a definite temperature the change in concentration of the enzymes has no influence on the equilibrium but only on the velocity; the latter, as in other catalytic actions, is directly proportional to the enzyme concentration.

5<sup>th</sup>. that as already observed by HENRI, the intensity of the invertase is smaller in proportion as the quantity of invert-sugar, present with the same amount of saccharose, is greater.

6<sup>th</sup>. that the intensity not only depends on the quantity of invert-sugar but also on the quantity of saccharose present in the solution; it is smaller when this quantity is greater.

This last conclusion does not agree with that of HENRI (Théses, p. 72) where he states that the addition of saccharose at the commencement of a reaction has no influence on the velocity of the inversion, but accelerates it when the addition takes place in the middle of a reaction.

7<sup>th</sup>. that, as duly required by theory, the reversal of the reactions between glucose and fructose and between glucose and saligenin proceeds very slowly and requires several weeks.

The results of HENRI's experiments are in accordance with the intensity formula, which I have deduced.

**Anatomy.** — “*The foetal membranes and the placenta of Phoca vitulina.*” By A. J. P. VAN DEN BROEK. (Communicated by Prof. L. BOLK).

(Communicated in the meeting of January 30, 1904).

Some time ago a seal in an advanced state of gestation was sent to the anatomical Laboratory of the Amsterdam University. As neither the foetal envelopes nor the placenta of the pinnipedal carnivores have been described in detail, I was very gratified to be entrusted by the Director of the Laboratory with the task of carefully examining these organs. The preparation turned out to be in very good condition and well enough preserved for microscopic examination.

Whereas a more detailed description will be published in another place, the following may be given here as the principal results of my investigations.

The gravid uterus was U-shaped, the convexity being on the cranial side. The organ, which was somewhat flattened dorso-ventrally was lying in transverse direction, so that the fundus uteri was situated in the righthand part of the body. This U-shaped curve was accompanied by a twisting of the organ, so that the left ovarium, entirely enveloped by an ovarial bag, was medially situated.

The greater part of the ligamentum latum had become absorbed; the ligamentum rotundum, a very powerful cord, ran from the front-, respectively hind-wall of the uterus, that is: from the spot where the ovarium was lying against the uterine wall, running down in a slanting direction across the latter, towards the abdominal wall. The ostium uteri, filled with a mucous clot, showed an aperture of  $\pm 3$  cm.

Close to the top of this ostium, which formed an oval foramen in the middle of the portio vaginalis, the foetal sac, rather strained, could be felt. All this seemed to indicate that the animal, being in labour, had gone ashore, when it was caught.

On opening the uterus by means of a longitudinal incision in the organ, along the convexity, the following was noticed: The wall of the uterus is extremely thin in proportion to the voluminous organ, a little more than 1 mm., but increases in thickness towards the vagina. The muscularis of the wall of the latter, however, is rather thick (1 cm.).

The chorion, as well as the placenta, is only loosely attached to the walls of the uterus all over. It appears that the foetal sac reaches down to the ostium uteri. On detaching the placenta I found septa of cellular tissue adhering to the inner surface of the wall of the uterus, which, just there, is somewhat thicker.

The placenta forms a perfectly closed girdle, situated about the middle of the foetal sac, or, with regard to the uterus, in the curve of that organ.

The uterine surface presents a lobated structure, the various irregular lobes being separated by pretty wide fissures, and as moreover, the placenta is comparatively thin, it is not very compact.

The circumference, measured at the surface of the uterus, is 66 cm., the width, which is the same all over, 32 cm. The edges are not stumpy and thick; rather thin. Several thick bloodvessels emerge from the sides of the placenta, branching off into the chorion so abundantly as to leave not a single part of it without a supply of vessels. On splitting the chorion and the placenta along the convex curve of the foetal sac, the amnion becomes visible. This is quite disconnected. There was no direct contact between the two tissues anywhere, nor with the placenta, the amnion not covering the foetal surface of the placenta, but branching off at the placental end of the umbilical cord. The amnion, like a bag with thin walls, invests the foetus pretty closely, especially along the back. Only behind the tail-end of the foetus, which is turned towards the fundus uteri, we find another part of the amnion that is not taken up by the foetus, but filled with a substance that is soft to the touch. The amnion is partly vascularized, partly devoid of any vessels; especially in the immediate vicinity of the umbilical cord a vascular part is noticeable. Here the amnion membrane seems also to be somewhat thicker and to consist of two layers, which are moveable one over the other. Here we find the umbilical sac, in the shape of an elongated organ, connected with the amnion right along, lying against this membrane.

As the amnion has not coalesced with the foetal surface of the placenta, the latter can be at once examined after opening the chorion. Of an insertion proper of the umbilical cord into the placenta there can hardly be any question, the vessels dividing and branching off long before they reach the placenta.

These ramifications enter the placenta at a rather considerable distance from each other. Slips of the allantois, which lines the placenta, cover these vessels, which therefore are found in duplicatures in this membrane as soon as they leave the cord. The main canals of each of the two umbilical arteries branch off into a girdle-shaped half of the placenta, and with fairly large ramifications spread further into the chorion. When the convex surface of the amnion is slit open very little foetal fluid runs out. The foetus is found to be lying with its muzzle towards the ostium

uteri, its back turned upwards. It also appears that the available space behind the tail-end of the foetus is filled up with about 3 liter of lanugo, some of which was also adhering in places to the body of the foetus. In the skin itself there were no remains of the lanugo-covering, which consisted of short, straight hairs, all of the same pearl grey colour. Speckled or black hairs were not found.

The umbilical cord has a length of only 12 cm. so that the animal, at the time of birth, is bound to pull out the placenta along with the membranes. The skin is continued for about 1 cm. along the umbilical cord, which is compressed sideways along its whole length. Taking into consideration the thickness of the umbilical cord there is only a small quantity of connective tissue. The three umbilical vessels are not twisted around each other. The outer surface of the umbilical cord is yellowish, shining, and feels hard.

A microscopical examination gave the following results:

The umbilical cord is covered with an epithelium forming a pavement of several layers, which forcibly reminds one of the epithelium of the epidermis. The lower layer of cells consists of high cells of a somewhat cylindrical shape, lying close together, with large round nuclei. Towards the surface the cells grow flatter, their limits being well defined in the layers immediately following the basal one. As the cells flatten down, the nuclei grow less prominent. Finally, forming the outside layer, there is a horny surface with lamelliform structure, in which, (by means of staining with haematoxyline) the remains of nuclei can be traced in places. This horny layer is sharply marked off from the epithelium-layer.

Where the amnion leaves the umbilical cord, this epithelium of many layers changes into a simple epithelium.

In the cord itself there are in section five channels of unequal width and with a wall of uneven thickness.

The two umbilical arteries and the vena umbilicalis have a very thick muscular coating of circular muscle-fibres. The muscle-cells show a lamelliform arrangement, the lamelli being separated by connective tissue.

Elastic filaments cannot be traced. Towards their lumen the blood-vessels are covered with an intima, which is not clearly defined towards the periphery.

In the walls of the blood-vessels we find, almost right up to the intima, the lumina of vasa vasorum, belonging to the system of the vessels proper of the umbilical cord, to be mentioned presently.

A fourth lumen is that of the second vena umbilicalis. The wall of it clearly shows an intima, round this there is a circular muscular

coating, and then, right round this, a coating of bundles of muscles running lengthways, but not adhering close together. In the walls of this vena I have not noticed any bloodvessels. In the lumen I found here and there some blood-corpuseles. In following up this partly obliterated vena towards the foetus, it is found to divide itself into two branches shortly before the foetal insertion of the umbilical cord; the two branches run together a little way down, then one of them splits up again and three branches can be traced right up to the front abdominal wall, where they lose themselves. Towards the placenta this vena also splits up into ramifications, which grow finer and finer and finally branch off into the tissue of the umbilical cord.

The fifth lumen in the umbilical cord is situated in the foetal half between the two umbilical arteries; towards the placenta these approach each other and the vessel runs alongside of them. This lumen is of an irregular shape, somewhat compressed and provided with an epithelium composed of cells that are flattened and arranged in several layers, the respective limits not being distinctly defined.

This lumen runs right through the cord till close to the placenta where it suddenly stops. There is no communication between this lumen and the yolksac. That we have here a continuation of the allantois-channel is proved by its original position between the two umbilical arteries, which position I also noticed inside the abdominal wall. I did not notice any remains of a yolk duct with certainty.

The stroma of the umbilical cord consists of cellular tissue with exceedingly fine fibrils pursuing a circular course. Underneath the epithelial coating this circular direction is deviated from and the curve becomes irregular. Round the vessels there is no distinct system of circular fibres. Between the two arteries the character of the stroma changes somewhat, it is of a looser construction and contains a few longitudinal bundles of smooth muscular tissue. These can best be seen by staining with polychrome methylen-blue (Unna) and can be traced right through the whole cord. By the side of this the profusion of the bloodvessels belonging to stroma funiculi proper seems remarkable.

These *vasa propria funiculi umbilicalis* are met with right along the funiculus, most of all in the foetal part. They appear to be connected with the vasa of the subcutaneous cellular tissue of the abdominal wall. Arteries as well as large veins filled with blood are noticeable. The distribution is somewhat irregular. Especially round the umbilical vessels they are heaped up together, entering the walls close up to the intima. I have not been able to ascertain the existence of a connection between the *vasa propria funiculi* and the *vasa*

umbilicalia. As far as I know, a case of the presence of vasa propria funiculi in any animal was not on record.

This isolated case suggests the general peculiarity of the vascular system of seals, to which attention has already been drawn by HYRTL<sup>1</sup>). I may add that the immediately surrounding parts of the allantois were also very rich in vasa propria, which, however, were generally of smaller size.

A microscopic examination of the chorion, or rather of the wall of the outermost and widest embryo-sac, shows us that there are two layers, an outer one and an inner one, connected by extremely loosely woven cellular tissues; between the two layers the blood-vessels are situated. The outer, or uterine layer, the chorion proper, is lined with a simple cylindrical epithelium about 20  $\mu$  high. The nuclei are oval-shaped and in the basal half of the cell; the protoplasm is finely granulated. Cell limits are distinctly visible. The inner lining consists of one layer of flat cells with much-flattened nuclei. The inner coat is nothing but the outer surface of the allantois. (This connection will be referred to by and by). We cannot, therefore, call this membrane the chorion, strictly speaking, the name of outer foetal envelope is more to the point. The bloodvessels in the wall of this sac are of unequal caliber, in the centre, between the two layers, larger vessels are met with, the arteries have a thick muscular coating, smaller vessels are found partly in the stroma of the allantois, in greater quantity however right under the chorion-ectoderm.

Even with the naked eye an accumulation of small villi, conspicuous by their velvety aspect, could be seen in some places on the uterine surface of the outer foetal sac. A microscopic examination confirmed that these were rudimentary villi. The epithelium did not differ from the other parts, but the stroma was a much more compact tissue and the interior was filled with very numerous capillaries the central ones of which had a fairly large lumen.

The amnion, too, or rather the inner foetal sac, is found to consist of two layers, lying against each other along the whole surface; only where the umbilical vesicle is situated they separate to envelop this. The inner layer is covered with a cubic epithelium of 10  $\mu$ ., the outer one is identical with the inner layer of the outer foetal sac and must be considered to be a layer of the allantois. On comparing foetal sacs of *Phoca vitulina* with those of other carnivores, *Phoca*

<sup>1</sup>) HYRTL. Ueber einige Eigentümlichkeiten der arteriellen Gefässverästelungen bei den Seehunden.

Sitz. Ber. d. math. naturw. Classe d. Akad. d. Wissensch. Vienna. B<sup>1</sup>. XI. 1854.

is found to exhibit somewhat different conditions. In dogs, for instance, according to the investigations of BISCHOFF <sup>1)</sup>, STRAHL <sup>2)</sup> and others, the allantois-sac forces its way between the chorion and the amnion. While the allantois is thus making its way further and further between the two membranes, gradually separating them almost entirely, the edges of the allantois are coming closer together. But these edges, according to the drawings of BISCHOFF (l.c. Plate XV, fig. 8) remain separated; according to STRAHL <sup>3)</sup>, they establish contact by means of cellular tissue, chorion and amnion being thus connected at this point of contact. In *Phoca* I found neither the edges of the allantois-sac, nor a connection like STRAHL noticed in dogs; I must therefore assume that in *Phoca* the development has gone a little further and that through the elimination of the partition between the two edges of the allantois-sac, mentioned by STRAHL, the outer and inner sac have become entirely isolated. The whole of the original extra-embryonal coelom-cavity has in this way disappeared; the space between the inner and outer foetal sac is the allantois-cavity.

I have already pointed out that the umbilical cord was connected with the placenta by means of a so-called insertio velamentosa. The vessels running towards the placenta or in the inverse direction, are enclosed by the membrane covering the foetal side of the placenta, viz. the outer layer of the allantois-sac, which continues on the chorion along the edge of the placenta.

As far as the inner foetal membrane is vascularised, the vessels show the same proportions as in the outer foetal sac.

The umbilical sac is situated in the inner wall of the foetal sac, between the amnion and the allantois, connected by thin cords of cellular tissue with both. It is a much-elongated, narrow bag, with folded walls.

The walls consist of strongly vascularized connective tissue, its limits are not sharply separated from the stroma of the amnion- and allantois membranes. Only here and there we find the remains of an original coating of epithelium. The bloodvessels, some of which have a fairly large lumen, run almost entirely lengthways through the organ. The majority of these vessels have a thick muscular wall and were filled with blood. These vessels and the umbilical ones are connected with one another.

With regard to the placenta the following may here be stated.

<sup>1)</sup> BISCHOFF, Die Entwicklungsgeschichte des Hundeëies.

<sup>2)</sup> STRAHL, Untersuchungen über den Bau des Placenta. III. Archiv für Anatomie und Entwicklungsgeschichte. 1890.

<sup>3)</sup> l.c. p. 199.

As already mentioned, the seal has a placenta zonaria, which, compared with that of the dog or the cat, is of much looser construction. The uterine side shows many more or less deep grooves, which divide the organ into a number of lobes. The deeper grooves, as a rule, run through the placenta in a longitudinal direction.

In the seal a green border-zone, such as we find described in the placenta of several carnivores, does not exist. Yet there is something like it. On detaching the placenta from the wall of the uterus, one could see, even with the naked eye, that both edges of the placenta were freely dotted with small, light-orange coloured particles, some as large as a pin's head; found, on examination, to consist of bilirubine. This pigment was found in enormous quantities and a microscopical investigation showed that the whole edge was saturated with these orange coloured bits. Owing to them, the narrow border-seam, instead of being a dark red, like the other parts of the placenta, was of a dirty brown colour.

As far as the blood-pigment penetrates in the placentary tissue — for these corpuscles may safely be taken to be transformed blood — the whole tissue, when seen under the microscope, is tinged a light yellow.

On following up this tinged zone under the microscope, we shall see that along the outer edge the amorphous pigment is found in great quantities, but no newly ejected blood is found. Only at some distance from the edge the clots of pigment become smaller, but at the same time they are found to be lying in ejected blood that can still be easily recognised as such, until finally, at the placental end of the brown zone, the blood predominates and here and there a glittering orange-coloured pigment clot is met with.

From this we may infer that the hemorrhage, during the development of the foetus, first occurs on the outer limits of the placenta and gradually more towards the centre.

The bleedings at the edge are not the only ones I noticed in the placenta.

In dogs, for instance, STRAHL describes some so-called green islets in the placenta, spots corresponding to the green edge-zone. These islets do not occur in seals either, at least they are not visible macroscopically. Under the microscope, however, we can see in many places, under the foetal coating of the placenta, some uniformly coloured light yellow spots. On close inspection it is seen that in such places, situated immediately below the foetal surface, hemorrhage has taken place, and that round this seat of bleeding the placental tissue is of a light yellow hue all over. Blood-pigment in

amorphous condition I have not been able to trace in such spots. The discoloration of the tissue may be explained in this way that the blood-corpuseles give off their haemoglobine to the surrounding parts and that this is absorbed gradually by the surrounding placenta-tissue. This latter point is the most significant part of the process, for, why should this surrounding tissue, which, unlike the corpuseles, can hardly be regarded as having died off, absorb the altered blood-pigment so uniformly? That we have here no post-mortem phenomenon appears clearly on examination of the blood-vessels at the edge of the placenta. As already stated, this is of a more intense yellow hue than that of the spots under the foetal surface, partly through the more considerable amount of pigment. Now, we find in the tissue of the border of the placenta, several vessels, the lumen of which, in addition to blood-corpuseles, is filled with pigment. These are foetal vessels. In the vasa umbilicalia I only found some blood, but no pigment.

The presence of this pigment in the vessels proves, that this yellow hue of the placenta-tissues is a vital reabsorption-process, and not one of post-mortem diffusion. There is another fact in favour of this view: it is my discovering (in the border-zone, where the villi are not very much elongated and the villous epithelium, or chorion ectoderm, is still intact), some distinct pigment-particles in these cells, which had been absorbed from the pigment situated close against this epithelium.

And on further comparing the structure of the placenta of Phoca with that of fissipede carnivores (e. g. the dog), it is found that the spongy layer is entirely missing; all along the thickness of the placenta the same uniform structure is maintained.

The foetal surface of the placenta is covered with a layer of the allantois, coated with a single layer of flat endothelium, as already described. Underneath this, there is a thin layer of fairly firm connective tissue, in which the larger ramifications of the umbilical vessels are found.

From this tissue coarse septa of connective tissue find their way into the placenta, which gradually diminish as they run towards the foetal surface, although they usually succeed in reaching it. In these septa the ramifications of the foetal vessels are found. Coarse septa send out finer compartments in every direction. The coarser ones divide the very compact mass of placenta into smaller sections.

From the maternal side too, some septa of connective tissue filling up the aforesaid grooves on the foetal side of the placenta, enter the latter; they are however less voluminous than those coming

from the foetal side. The compact cellular tissue of the placenta reaches right up to the wall; between the latter's coating of muscles and the compact placenta tissue a very narrow, loosely woven layer of connective tissue runs. In this layer, lying against the muscular coat, we find the diameters of the very wide uterine vessels and also in several places some uterus-glands. These glands, in the shape of elongated tubes with short ramifications and parallel with the surface of the uterus, are squeezed in between the muscular coat and the placenta. They have a distinct lumen, the epithelium is highly cylindrical. They are glands that have obviously fully developed, but have not been invaded by villi. On the foetal surface of the placenta moreover, distinct extremities of glands are met with, which, like those just described, have bent round and which run parallel with the muscular coat, in which a foetal villus is plainly visible. These villi are not lying close to the inner surface of the follicle, but are somewhat retracted from it. I did not succeed in observing a distinct epithelium on these villi.

Some of these uterus glands appear in another form: the cells have very much increased in volume, have swollen and are bulging out in several places in the lumen. The protoplasm of these cells is of a well defined reticular structure, the cell nuclei are in the basal part of the cells. In the lumen of such glands we find some independent cells, or combinations of only a few, some with nuclei, the larger ones without any; moreover some conglomerations of deeply stained fine particles may be observed here and there.

The compact mass of the placenta, when magnified, turns out to contain a great number of bloodvessel-lumina, adhering close together, each one of them surrounded by a distinct endothelium-wall. The ramifications of the foetal vessels, together with some connective tissue, run between these branches of the placental vessels. Forming a separating layer between these two systems of blood-vessels, we find in the greater part of the placenta one single layer of nuclei, situated in a mass of protoplasm, in which, however, no cell limits could be traced. This layer of nuclei, is to be regarded as belonging to a syncytium. In some places I counted two, sometimes even more, rows of nuclei between the branches of the placental- and those of the foetal vessels, without my being able to say with certainty which part of it should be taken to be of a syncytial character.

In the cases of suballantoidal hemorrhage and in the surrounding parts, the nuclei of cells, lining the endothelium-walls of placental vessels and the foetal villi adhering to the blood-mass, are of a much darker hue than those of other parts of the placenta. As a

coating of these foetal villi I often observed a double layer of nuclei, viz. a layer of flattened nuclei, lying close together, coating the villus and, round this, a layer of round, large nuclei. Against the latter layer the extravasated blood is found. Between the nuclei of the inner series, cell-limits are sometimes noticeable (chorionectoderm).

Finally I want to offer a few remarks about the villi in the border-seam.

The mass of coagulated blood found near the edge of the placenta, and the bulk of which has the shape of amorphous, orange coloured lumps, is mainly situated between two very long villi, running in a slanting direction from the foetal surface of the placenta to the wall of the uterus. From these villi and from the part of the chorion that is lying between the bases of the two, a number of shorter villi, with ramifications, find their way into the above mentioned mass.

These villi are generally somewhat swollen and rounded off at their extremities. They are all conspicuous by their profuse vascularity.

The chorion between the bases of the two villi just described is covered with a layer of very darkly-stained nuclei, lying very close together. It remains doubtful whether this was a syneytium.

The secondary villi, passing into the above mass also have such a coating. In some cases two rows of nuclei could be seen on the surface, while it seemed to me that the row of nuclei turned towards the villus was not of such a dark hue as the outer one turned towards the blood-mass. At the extremities of the villi the nuclei are found to lie very closely together and to be more numerous.

Both in the protoplasm of the latter layer, covering the chorion, and in that of the villi one observes accumulations of orange-coloured particles.

Reabsorption of these corpuscles from the mass found in the border-seam of the placenta is therefore effected by means of the coating of the said layer of the chorion as well as that of the villi.

In one or two instances I found a coloured particle in the stroma of a villus or in the capillaries running into it.

**Mathematics.** — “On the differential equation of MOXGE” by Prof. W. KAPTEYN.

(Communicated in the meeting of January 30, 1904).

If we suppose that in the differential equation

$$Hr + 2Ks + Lt = 0 \quad \dots \quad (1)$$

$H, K, L$  depend only on  $p$  and  $q$ , the necessary and sufficient conditions for the existence of two intermediate integrals are the following.

In the first place  $H, K$  and  $L$  must be proportional to the second differential coefficients of a function  $\theta$ ; thus

$$\frac{H}{\theta_{11}} = \frac{K}{\theta_{12}} = \frac{L}{\theta_{22}} \quad \dots \quad (2)$$

In the second place the function  $\theta$  must satisfy the differential equation of the fourth order

$$\begin{aligned} & 2D \left( \theta_{22} \frac{\partial^2 D}{\partial p^2} - \theta_{12} \frac{\partial^2 D}{\partial p \partial q} + \theta_{11} \frac{\partial^2 D}{\partial q^2} \right) = \\ & = 3 \left[ \theta_{22} \left( \frac{\partial D}{\partial p} \right)^2 - 2\theta_{12} \frac{\partial D}{\partial p} \frac{\partial D}{\partial q} + \theta_{11} \left( \frac{\partial D}{\partial q} \right)^2 \right] \quad \dots \quad (3) \end{aligned}$$

where

$$D = \sqrt{\theta_{12}^2 - \theta_{11} \theta_{22}}$$

The general integral of this differential equation can be represented by the following formulae:

$$\left. \begin{aligned} p &= \frac{g' - h'}{u - v} \\ q &= \frac{\varphi' - \psi'}{u - v} \\ \theta &= 2 \int g' \varphi'' du - 2 \int h' \psi'' dv - (g' - h') (\varphi' + \psi') - \\ & - \frac{2}{u - v} \left[ (g - h) (\varphi' - \psi') - (\varphi - \psi) (g' - h') \right] \end{aligned} \right\} \quad \dots \quad (4)$$

where  $u$  and  $v$  indicate arbitrary parameters and

$$g = g(u) \quad , \quad h = h(v) \quad , \quad \varphi = \varphi(u) \quad , \quad \psi = \psi(v)$$

four arbitrary functions, and

$$g' = \frac{dg}{du} \quad , \quad g'' = \frac{d^2g}{du^2} \quad \text{etc.}$$

If the conditions (2) and (3) are satisfied the equation (1) will possess the two intermediate integrals

$$\begin{aligned} z - z \varphi'' - x g'' &= \bar{\delta}(u), \\ z - y \psi'' - x h'' &= \bar{\delta}(v), \end{aligned}$$

where  $\tilde{\kappa}$  denotes an arbitrary function and  $u$  and  $v$  the functions of  $p$  and  $q$ , derived from the equations (4).

In the particular case that the function  $\theta$  satisfies the two members of the equation (3) separately, we have to distinguish two cases according to the double sign in

$$\frac{\partial D}{\partial q} - \frac{\theta_{12} \pm \sqrt{\theta_{12}^2 - \theta_{11} \theta_{22}}}{\theta_{11}} \frac{\partial D}{\partial p} = 0.$$

The general integral can be written in both cases respectively

$$\left. \begin{aligned} p &= \frac{1}{u} f[u(v \mp g'')] + r''(u) \\ q &= v \\ \theta &= (2u^2 g'' - 4u g' + 4g \mp u^2 v) p - 2 \int (u g''' \mp v) u p \, du \end{aligned} \right\} . \quad (5)$$

where  $g = g(u)$  has the same meaning as before, whilst  $f$  and  $r$  represent two new arbitrary functions of the arguments placed after these symbols.

In these cases the two intermediate integrals are

$$\begin{aligned} z \mp y(u g''' - g'') - x(ur''' + r'') &= \tilde{\delta}(u), \\ y + x f''[u(v \mp g'')] &= \tilde{\delta}[u(v \mp g')], \end{aligned}$$

the values of  $u$  and  $v$  being expressed in  $p$  and  $q$  with the aid of the formulae (5).

The condition (3) appears, although in a different shape, already in the excellent dissertation of J. VÁLYI (Klausenburg 1880).

**Mathematics.** — “*The singularities of the focal curve of a plane general curve touching the line at infinity  $\sigma$  times and passing  $\varepsilon$  times through each of the imaginary circle points at infinity.*”

By Dr. W. A. VERSLUYS. (Communicated by Prof. P. H. SCHOUTE).

(Communicated in the meeting of January 30, 1904).

In “Verhandeling” 5 of the “Kon. Ak. v. W.” at Amsterdam Vol. VIII, I have deduced some formulae expressing the singularities of the focal developable and of the focal curve in function of the singularities of a plane curve having no particular position.

In a similar way it is possible to deduce the following formulae expressing the singularities of the focal developable and of the focal curve of a plane curve touching the line at infinity  $\sigma$  times and

passing  $\varepsilon$  times through each of the imaginary circle points at infinity.

Let the plane curve be of order  $\mu$ , of class  $\nu$  and let  $\iota$  represent the number of its inflectional points. Then the singularities of the evolute or of the cuspidal curve of its focal developable are the following:

rank,  $r = 2(\mu + \nu - 2\varepsilon - \sigma)$

class,  $m = 2\nu$

number of stationary planes,  $a = 2\iota$

double osculating planes,  $G = \nu^2 - \nu - \mu - 3\iota + 3\sigma^2 + 2\varepsilon - \sigma$

stationary tangents,  $v = 0$

double points,  $H = 3(\mu - \nu) + \iota$

double tangents,  $\omega = 0$

order,  $n = 2(3\mu + \iota - 6\varepsilon - 3\sigma)$

stationary points  $\beta = 2(6\mu - 2\nu + 3\iota - 12\varepsilon - 6\sigma)$

stationary points not at infinity and not in the plane of the curve

$$\beta' = 2(5\mu - 3\nu + 3\iota - 8\varepsilon - 3\sigma)$$

order of the nodal curve  $x = 2(\mu + \nu)^2 - 10\mu - 2\nu - 3\iota - 8\mu\varepsilon$   
 $- 4\mu\sigma - 8\nu\varepsilon - 4\nu\sigma + 8\varepsilon^2 + 8\varepsilon\sigma + 2\sigma^2$   
 $+ 20\varepsilon + 10\sigma.$

The chief singularities of the focal curve are:

order,  $n = 2\mu^2 + 4\mu\nu + \nu^2 - 11\mu - \nu - 3\iota - 8\mu\varepsilon - 4\mu\sigma - 8\nu\varepsilon - 2\nu\sigma$   
 $+ 8\varepsilon^2 + 8\varepsilon\sigma + \sigma^2 + 20\varepsilon + 9\sigma$

rank,  $r = 4\mu\nu + \nu^2 - 4\mu - 4\nu - 8\varepsilon - 2\nu\sigma - 3\sigma^2 + 8\varepsilon + 5\sigma$

number of stationary tangents,  $v = 0$

class,  $m = 6\mu^2 + 6\mu\nu + 4\mu + 2\nu - 36\mu - 12\nu - 18\iota - 24\mu\varepsilon$   
 $- 6\mu\sigma - 12\nu\varepsilon - 4\nu\sigma - 8\varepsilon - 2\sigma + 24\varepsilon^2 + 12\varepsilon\sigma - 8\sigma^2$   
 $+ 60\varepsilon + 28\sigma$

number of stationary points  $\beta = 2(3\mu + \iota)(2\mu + \nu) - 57\mu + 21\nu$   
 $- 27\iota - 48\mu\varepsilon - 18\mu\sigma - 12\nu\varepsilon - 4\nu\sigma$   
 $- 8\varepsilon - 2\sigma + 48\varepsilon^2 + 36\varepsilon\sigma + 4\sigma^2$   
 $+ 36\varepsilon\sigma + 96\varepsilon + 40\sigma.$

**Mathematics.** — “On the position of the three points which a twisted curve has in common with its osculating plane.” By Dr. W. A. VERSLEYS. (Communicated by Prof. P. H. SCHOUTE.)

(Communicated in the meeting of January 30, 1904).

§ 1. Let  $d$  be the section of the osculating plane  $V$  in a point  $P$  of the twisted curve  $C$  with the developable  $O$  of which  $C$  is the cuspidal curve; then the twisted curve  $C$  and the section  $d$  have in the point  $P$  only two points in common, that is they have in  $P$  a contact of the first order.

The curve  $C$  has in  $P$  three successive points in common with the plane  $V$ . The curve  $C$  is situated on the surface  $O$ , so the three common points must lie on the section of  $O$  with  $V$ . This section consists of the curve  $d$  and of the common tangent  $l$  in  $P$  of  $C$  and  $d$ , counting double. In the following way can be proved that of the three common points only two lie on  $d$ .

Let us first take instead of a general curve a twisted cubic  $C_3$ . Let  $P$  be the origin; the property being projective the plane at infinity can be chosen in such a way, that the curve is represented by the equations

$$x = t^2, \quad y = t^2, \quad z = t.$$

If now in point  $t=0$  the curves  $C_3$  and  $d_2$  had three common points then in the origin also the radii of curvature of the two curves would be the same. Let  $R$  be the radii of curvature of  $C_3$  in  $P$  and  $r$  the radius of curvature of  $d_2$  in  $P$ , we then easily find:

$$R = \frac{ds^3}{\sqrt{\{A^2 + B^2 + C^2\}}} = \frac{(1 + 4t^2 + 9t^4)^{3/2}}{\sqrt{\{4 + 36t^2 + 36t^4\}}}.$$

So for  $t=0$  we find  $R = \frac{1}{2}$ .

The surface  $O_4$  is enveloped by the plane

$$x - 3yt - 3zt^2 - t^3 = 0.$$

So the curve  $d_2$  is enveloped by the line

$$-3y + 3zt - t^2 = 0$$

Consequently the equation of  $d_2$  is

$$y = \frac{3}{4}z^2.$$

so the radius of curvature  $r = \frac{2}{3}$ . The curves  $C_3$  and  $d_2$  have in the origin not the same radius of curvature, so they have not three or more points in common.

Let  $p$  be the orthogonal projection of  $C_3$  on  $V$  ( $x=0$ ), then  $C_3$  has with  $p$  three successive points in common in  $P$ , for all points which  $C_3$  has in common with  $V$  must lie on the section  $p$  of  $V$  with the projecting cylinder of  $C_3$ . The projection  $p$  has for equation

$$y = z^2,$$

and so also the radius of curvature in the origin  $R = \frac{1}{2}$ , showing again that the curves  $p$  and  $C_3$  have in the origin three points in common.

Out of the two values  $R = \frac{1}{2}$  and  $r = \frac{2}{3}$  ensues that the section  $d_2$  lies near  $P$  on the convex side of the projection  $p$ .

§ 3. The latter can also be proved as follows for any curve with the aid of Descriptive Geometry.

If we take the osculating plane  $V$ , in any point of the curve  $C_3$ , to be the vertical plane of projection and the normal plane of the curve to be the horizontal one (plane of projection), then the vertical projection  $p''$  is a curve cutting the axis perpendicularly in a common point  $P$  and the horizontal projection  $p'$  is a curve having in  $P$  a cusp with the axis for cuspidal tangent. Let us now construct the vertical trace  $d''$  of  $O$ . The vertical traces of the generating lines of  $O$  lie on the tangents to  $p''$ , thus all on the convex side of  $p''$ , whilst those traces are also situated on the same side of the perpendicular on the axis in  $P$ , where also  $p''$  and  $p'$  are lying. So the curves  $d''$  and  $p''$  turn the concave side to the same side, whilst  $d''$  near  $P$  lies outside  $p''$ . So the curves  $d''$  and  $p''$  have an even number of points in common.

Thus if  $C$  and  $d''$  had the three points of  $C$ , lying in  $V$ , in common, then also  $p''$  and  $d''$  would have three points near  $P$  in common. So according to what was proved above  $p''$  and  $d''$  had four points in common. That fourth common point of  $p''$  and  $d''$  would, lying on  $d''$ , also lie on  $O$  and would be the projection of a point  $Q$  of the curve  $C$  lying as near to it as one desires. So at the limit the projecting line of  $Q$  would be a tangent of  $O$ . Thus near  $P$  a tangent of  $O$  might be perpendicular to the osculating plane  $V$ , which is impossible. So  $C$  and  $d''$  have no three points in common.

§ 4. We can prove moreover as follows synthetically that the twisted cubic  $C_3$  has not three points in common with the trace  $d_2$ .

If  $C_3$  and  $d_2$  had three points in common at  $P$  then  $d_2$  and the projection  $p_3$  of  $C_3$  on  $V$  out of any arbitrary point  $A$  would have three successive points in common. This projection  $p_3$  is a cubic curve of class four. The three inflexional tangents of  $p_3$  are the traces of the three osculating planes through  $A$ , thus they are also tangents to  $d_2$ . As the contact of the second order in  $P$  must count for three common tangents and each of the three inflectional tangents of  $p_3$  for two common tangents, two curves respectively of class two and class four would have nine common tangents, which is impossible. So the curves  $C_3$  and  $d_2$  have at  $P$  no three points in common.

§ 5. It follows from what was proved above for a twisted cubic that also a general twisted curve  $C$  has not more than two points in common with the section  $d$  of its developable  $O$  and the osculating plane  $V$ . If  $C$  and  $d$  had three points in common, then  $d$  and the projection  $\rho$  of  $C$  out of any arbitrary point  $A$  on the plane  $V$  of  $d$  would have three points in common. Let  $C_3$  be a twisted cubic having in  $P$  six successive points in common with  $C$ . Now  $V$  is also the osculating plane of  $C_3$  in  $P$ ; let  $d'$  be the trace of the developable  $O_4$  belonging to  $C_3$  and let  $\rho'$  be the projection of  $C_3$  on  $V$  out of  $A$ . As the developables  $O$  and  $O_4$  have five successive generating lines in common, so  $d$  and  $d'$  have at least three successive points in common, whilst  $\rho$  and  $\rho'$  have six successive points in common. Now, if  $d$  and  $\rho$  had three successive points in common at  $P$ , this would also be the case with  $d'$  and  $\rho'$ . According to the preceding § the latter is not true, so  $C$  and  $d$  have neither three points in common.

§ 6. The theorem can also be proved by searching for the points of intersection of the cuspidal curve  $\nu$  or of the nodal curve  $\xi$  with a second polar surface  $\Delta^2 O$ , just as CREMONA did (CREMONA—CURTZE; p. 87—90). To simplify the matter I shall first apply this proof to a twisted cubic, after which the proof for the general case can be more easily followed.

Let us take for developable  $O$  the surface consisting of a developable  $O_4$  and of a quadratic cone  $K$  with vertex  $T$ , passing through the conic  $d_2$  situated in the osculating plane  $V$  of  $P$  and on  $O_4$ . The cuspidal curve of this surface of order six is the cuspidal curve  $C_3$  of  $O_4$ , so  $\nu = 3$ . The nodal curve  $\xi$  consists of  $d_2$  and of a curve of order six  $s$ . This curve  $s$  intersects the plane  $V$  of the conic  $d_2$  six times, three times of which in the points where  $d_2$  meets a generating line of  $O_4$ , for which the tangent plane passes through  $T$ , these three points being points of contact of double tangent planes of  $O$ . Consequently  $s$  has in  $P$  three successive points in common with  $d_2$ . Let  $\Delta^2 O$  be the second polar surface for a point  $A$  lying in  $V$ . The order of  $\Delta^2 O$  is four.

In the formula of CREMONA for  $\xi(q-2)$  I have only to keep the first and the third term, none of the singularities appearing on the surface under consideration which are furnishing the other terms; but a term  $P$  must be added for the particular point  $P$  where another third sheet of the surface  $O'$  passes through a plane curve  $d_2$  lying on  $O_4$ . This singularity has not been considered by CREMONA;

it appears on the focal surface of a plane or twisted curve touching the plane at infinity.

So the formula of CREMONA becomes :

$$s(\varrho - 2) = \text{number of times that } s \text{ meets the curve} \\ \text{of contact of } A + 3\lambda + P.$$

The curve of contact of  $A$  consists of the generating lines of  $O'$  of which the tangent plane passes through  $A$ . Of these generating lines two are situated on the cone  $K$ , each of these meeting the curve  $s$  three times and two are situated on  $O_4$  as  $A$  lies on the osculating plane  $V$ ; the latter meet  $s$  each one time. This number of points of intersection of  $s$  with  $\Delta^2 O'$  is thus eight. According to CREMONA they must each be counted one time, so the first term is 8.

The section of  $O'$  with  $V$  consists of  $d_2$  and of the tangent in  $P$  to  $d_2$ , both counted double. So the second polar curve of  $A$  for this curve or the section of  $V$  with  $\Delta^2 O'$  consists of a curve of order four, touching  $d_2$  twice in  $P$ , having thus with  $d_2$  and with  $s$  too only four points in common. The formula of CREMONA gives :

$$6 \times 4 = 8 + 3 \times \lambda + 4.$$

Consequently :  $\lambda = 4$ .

The points  $\lambda$  are the points outside  $P$  where the cuspidal curve meets another sheet. As  $C_3$  meets the cone  $K$  in all six times,  $C_3$  can meet the cone  $K$  in  $P$  only twice, so  $C_3$  has also with the curve  $d_2$  lying on  $K$  but two points in common.

§ 7. If we had taken  $A$  outside the plane  $V$  this change would have had no influence on the number of points  $\lambda$ , but the term issuing from the lines of contact would have been one more, so  $P$  would in that case have counted for 3.

By applying the above used method to the nodal curve  $d_2$ , we find that  $\Delta^2 O'$  of an arbitrary point  $A$  lying outside  $V$  also meets  $d_2$  in three points. The singularity  $P$  counts for six points of intersection of the total nodal curve  $\xi$  with  $\Delta^2 O'$ , thus for as many points of intersection as two points  $\lambda$ .

Out of the formula of CREMONA for  $r(\varrho - 2)$  it is evident that  $P$  counts for two points of intersection of the cuspidal curve  $C_3$  with  $\Delta^2 O'$ , thus also for two points  $\lambda$ . From what precedes ensues that the cone  $K$  passing through  $d_2$  is an ordinary touching cone and that the point of contact  $P$  counts in both formulae of CREMONA for two points  $\lambda$ .

§ 8. Let the curve  $C$  be a general twisted curve of order  $r$ . Let  $O$  be its developable, the class  $\mu$ , the rank  $\varrho$  and let the order of

the nodal curve on  $O$  be  $\xi$ . Let the number of stationary tangents be  $\theta$  and that of the double tangents  $\omega$ . Let  $P$  be an ordinary point on  $C$ ,  $l$  the tangent in  $P$  to  $C$ ,  $V$  the osculating plane in  $P$  and  $d$  the curve of intersection of  $V$  with the surface  $O$ . Let  $c_2$  be a conic having at  $P$  five successive points in common with  $d$ . Let  $T$  be the vertex of a quadratic cone  $K$  passing through  $c_2$  where  $T$  is arbitrary but taken in such a way that  $K$  cuts the curve  $C$  in none of its singular points. Let  $s$  be the curve of intersection of  $O$  with  $K$ . This curve, of order  $2\varrho$ , shows singular points: 1<sup>st</sup> in  $P$ ; 2<sup>nd</sup> where  $C$  or a line  $\theta$  cuts the cone  $K$  (point  $P$  excepted), these are cusps  $\lambda$  on  $s$ ; 3<sup>rd</sup> where  $K$  meets the curve  $\xi$  or a line  $\omega$ ; these points are on the surface  $O'$  consisting of  $O$  and  $K$  triple points  $\tau$  and nodal points on  $s$ .

If we now determine the points of intersection of  $s$  with the second polar surface  $\Delta^2 O'$  of a point  $A$  lying in  $V$  then according to CREMONA the cusps  $\lambda$  must count three times and the triple points  $\tau$ , through which only two branches of  $s$  pass, must count twice. In order to find out for how many points of intersection the point  $P$  must count, we consider the first polar curve of the section of  $O'$  with  $V$ . This section consists of the right line  $l$  counted twice, of the curve  $d$  and of the conic  $c_2$ . So the first polar curve consists of the right line  $l$  and of a curve of which one branch has five points in common at  $P$  with  $c_2$  or with  $d$  and of a branch touching  $l$  also in  $P$  and lying at  $P$  between  $l$  and  $d$ . So the second polar curve shows at  $P$  two branches touching  $c_2$ . The two branches of  $s$  passing through  $P$  touch  $l$  in  $P$ , and  $V$  being also of both branches the plane of osculation, they have both with  $V$  or with  $c_2$  three points in common. Each branch of  $s$  through  $P$  has thus with  $\Delta^2 O'$  in  $P$  but four points in common, so that the point  $P$  counts for eight points of intersection.

Besides meeting the curve  $s$  in these singular points of  $s$  the polar surface  $\Delta^2 O'$  meets it moreover in the ordinary points where  $s$  meets the curve of contact of tangent planes through  $A$ . These points count according to CREMONA each one time. The curve of contact consists of two generating lines of  $K$  each meeting the curve  $s$   $\varrho$  times and of  $(\mu-1)$  generating lines of  $O$ , as  $A$  is situated in the osculating plane  $V$ . These generating lines each meet  $s$  two times, so that to determine  $\lambda$  we arrive at the formula:

$$2\varrho^2 = 3\lambda + 4\xi + 4\omega + 8 + 2\varrho + 2(\mu-1),$$

$$3\lambda = 2\{\varrho^2 - \varrho - \mu - 2\xi - 2\omega - 3\}.$$

As according to one of the formulae of CAYLEY-PLÜCKER

$$\rho^2 - \rho - \mu - 2\xi - 2\omega = 3(r + \theta),$$

then

$$\lambda = 2r + 2\theta - 2.$$

So the curve  $C$  meets the cone  $K$  outside  $P$  still  $2r - 2$  times, and  $P$  counts for two points of intersection. So the curve  $C$  also meets the conic  $c_2$  lying on  $K$  only two times and consequently the curve  $d$ , having with  $c_2$  five points in common at  $P$ , meets it also only two times.

**Chemistry.** — “*A contribution to the knowledge of the course of the decrease of the vapour tension for aqueous solutions.*”  
By Dr. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.)

1. In 1788 BLAGDEN<sup>1)</sup> discovered the relation between the lowering of the freezing point and the quantity of the solved substance. Among the substances which he examined, were however also some, which showed deviations, either in this sense that the lowering of the freezing point increased more rapidly or in that sense that it increased more slowly than the concentration.

RÜDORFF<sup>2)</sup>, who quite ignorant of BLAGDEN's work, made the same discovery in 1861, and COPPET<sup>3)</sup>, who ten years later (1871), continued RÜDORFF's investigations, came both to the result, that deviations from the rule first discovered by BLAGDEN, occurred both in one sense and in the other. A disproportionately rapid increase of the lowering of the freezing point with the concentration was found among others for NaBr, NaJ, CaCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and also for NaCl, whereas for the nitrates of Na, NH<sub>3</sub>, Ba, Ca, Sr, Pb, Ag and for Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>CNS the reverse was observed.

As an illustration of the course, as for NaBr etc. RÜDORFF had already adopted the formation of hydrates. COPPET assumed for the deviations for the nitrates, which are mostly anhydrous, that they are modified by the action of water or by the fall of the temperature in a certain, not further defined way.

Results analogous to those of BLAGDEN, RÜDORFF and COPPET were obtained by TAMMANN<sup>4)</sup> in 1887 when determining the decrease of the vapour tension. TAMMANN found namely, that for most of the salt

<sup>1)</sup> Wied. Ann. **39**, 1. (1890).

<sup>2)</sup> Pogg. **114**, 63. (1861); ib. **116**, 55 (1862); ib. **145**, 599 (1871).

<sup>3)</sup> Ann. Chim. Phys. (4) **23**, 366. (1871); ib. **25**, 502. (1872); ib. **26**, 98 (1872).

<sup>4)</sup> Wied. Ann. **24**, 523. (1885).

solutions the diminution of the vapour tension with increase of concentration increased more than the concentration, whereas for the nitrates of K, Na and for  $\text{KClO}_3$  the reverse was observed. The later investigations of BREMER<sup>1)</sup>, HELMHOLTZ<sup>2)</sup>, WALKER<sup>3)</sup> and DIETERICI<sup>4)</sup> gave the same result as those of their predecessors viz. this that in general the diminution of the vapour tension increases more rapidly than the concentration, and that the salts which form an exception to this rule are chiefly the anhydrous nitrates.

Up to 1903 the determinations of the freezing point of salt solutions of smaller concentrations than those which had been earlier investigated, yielded the result, that the molecular lowering of the freezing point *decreases* with increase of the concentration. As these measurements were continued to the concentration of  $\pm 1$  gr. mol. per 1000 gr.  $\text{H}_2\text{O}$ , it followed necessarily, that where the reverse course had been ascertained by the earlier observers, a minimum value had to occur in the molecular decrease of the freezing point, but for a concentration which lay above that where the investigators of later time had stopped.

In 1896, however, I had come to the conclusion in the determinations of the vapour tension by means of the micromanometer<sup>5)</sup>, that for dilute solutions, i.e. for solutions below the concentration of 1 gr. mol. per 1000 gr.  $\text{H}_2\text{O}$ , the molecular diminution of the vapour tension *increased* with the concentration. This was found inter alia for solutions of  $\text{NaCl}$ ,  $\text{KOH}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{CuSO}_4$ , whereas for  $\text{KNO}_3$ -solutions the reversed course was found. This result was therefore in perfect accordance with what had been found by my predecessors for more concentrated solutions, but was directly opposed (except  $\text{KNO}_3$ ) to the results of the determinations of the freezing point.

The question was now: "Which results are the correct ones?"

In the determination of the boiling point I hoped to find a means to answer this question. After having applied some improvements to the method and after having rendered myself independent of the fluctuations of the atmospheric pressure by using a *manostat*, I began the investigations and the result was published in April 1900<sup>6)</sup>.

1) Rec. tr. Chim. **6**, 122. (1887).

2) Wied. Ann. **27**, 568. (1886).

3) Zeitschr. f. phys. Chem. **2**, 602. (1888).

4) Wied. Ann. **42**, 513. (1893); ib. **62**. 616. (1897). Ann. phys. Chem. **27**, 4. (1898).

5) Archiv. Néerl. (2) 1 (1897).

6) These Proceedings II April 21 1900 p. 635, April 20 1901, III p. 717. In the same year (1900) JONES, CHAMBERS and FRAZER cryoscopically found minima for  $\text{MgCl}_2$  and  $\text{BaCl}_2$  lying at 0.1—0.2 gr. mol.

I arrived at the following result :

The molecular rise of the boiling point increased for solutions of NaCl and KCl from the concentration  $\pm 0.3$  gr. mol. per 1000 gr. H<sub>2</sub>O, both towards higher and towards lower concentrations, or in other words, the molecular rise of the boiling point proved to have a *minimum value* lying at  $\pm 0.3$  gr. mol. For the anhydrous nitrates of K, Na, Ba, Ag and Pb, however, the molecular rise of the boiling point proved, quite in concordance with the determinations of the vapour tension, to continually decrease with increase of the concentration.

The method which was the least accurate in appearance, proved to be able to point out a mistake both in the method of the freezing point and in that of the vapour tension. The first work was then to force the micromanometer to greater accuracy by applying some improvements, and then to repeat the experiments. In 1901<sup>1)</sup> a new series of experiments yielded really a result which qualitatively harmonized perfectly with that obtained by means of the boiling point method. For NaCl as well as for H<sub>2</sub>SO<sub>4</sub> a minimum occurred in the molecular decrease of the vapour tension, lying at  $\pm 0.5$  gr. mol. As before KNO<sub>3</sub>-solutions gave a strong decrease of *i* with increase of the concentration.

In the same year KAHLBERG<sup>2)</sup> found for solutions of NaCl, KCl, KBr, KJ and MgCl<sub>2</sub>, that the molecular rise of the boiling point increased continually with the concentration for the first and the last salt from the concentration  $\pm 0.2$  gr. mol. to  $\pm 5$  gr. mol., whereas for KCl, KBr and KJ a more or less clearly marked minimum was found.

BILTZ<sup>3)</sup> was the first to confirm my results with certainty in 1902. He found a minimum in the molecular rise of the boiling point, not only for KCl and NaCl, but also for RbCl and LiCl. His determinations of the freezing point of alkali chlorides showed only for LiCl a continual increase of the molecular lowering of the freezing point with the concentration; a minimum was not found, however, for the chlorides of the alkali metals by this method. For LiNO<sub>3</sub> and LiBr BILTZ found a faint minimum, whereas for the chlorides of the bivalent metals by the cryoscopic way very strongly pronounced minima were found, mostly lying between 0.1 and 0.2 gr.

<sup>1)</sup> These Proc. IV September 28 1901 p. 163.

<sup>2)</sup> Journ. Phys. Chem. 5, 339 (1901).

<sup>3)</sup> Zeitsch. f. Phys. chem. 40 s. 185 (1902).

mol., which is in accordance with the observations of JONES, CHAMBERS and FRAZER <sup>1</sup>).

The first who by the cryoscopic way discovered minima in the molecular lowering of the freezing point for chlorides of the alkali metals below the concentration 1 gr. mol., were JONES and GETMAN <sup>2</sup>), who published their results in the newly published *Jubelband für Ostwald*. It is remarkable that working with the common apparatus of BECKMANN these observers obtained more accurate results than RAOULT with his apparently ideal apparatus. For RAOULT found for NaCl-solutions up to the concentration 1 gr. mol. a regular decrease of the molecular lowering of the freezing point with increase of the concentration.

2. After having thus shortly pointed out what the boiling point method, the vapour tension method and the freezing point method have brought to light for the study of the non-diluted solutions, I proceed to give the results of the determinations of the diminution of the vapour tension of NaCl and NaNO<sub>3</sub>-solutions, made by means of the *micromanometer*, in which the aniline-water-manometer was replaced by the manometer of Lord RAYLEIGH <sup>3</sup>). It seemed namely very desirable for the greater certainty of the results, to repeat some measurements with another apparatus, the accuracy of which did not differ too much from that of my manometer. Lord RAYLEIGH'S invention was therefore very welcome to me, because his manometer was stated to reach an accuracy of  $\pm 0.00045$  m.m. Hg, and mine had an accuracy of 0.00025 m.m. Hg.

Lord RAYLEIGH'S manometer and the arrangement of this apparatus has been represented in fig. 1 and 2. *A* is a barometer tube, which branches into two parts at the top; the two branches are blown out to two bulbs of  $\pm 25$  mm. diameter at *BB*. In these bulbs extend two finely drawn out glass points, which are ground off to a sharp point at the lower end. On the tubes *LL*, of which the one more to the left is split up into two branches, as is seen in the horizontal projection, and which thus furnish three points of support, a glass plate *N* is laid which bears a mirror *M*, whose front is silvered. The glass plate *N* is fastened to the three points of support and the mirror *M* to the glass plate by means of water glass.

Lord RAYLEIGH had connected the tubes *CC* with his apparatus by means of straight glass tubes 3 meters long, but here some glass spirals  $\pm 35$  c.m. long have been added between them in order to prevent any wrenching.

<sup>1</sup>) Amer. chem. Journ. **23**, 89 (1900); ib. **23**, 512 (1900).

<sup>2</sup>) Zeitschr. f. Physik chem. **46**, 244 (1903).

<sup>3</sup>) Zeitschr. f. Physik chem. **37**, 713 (1901).

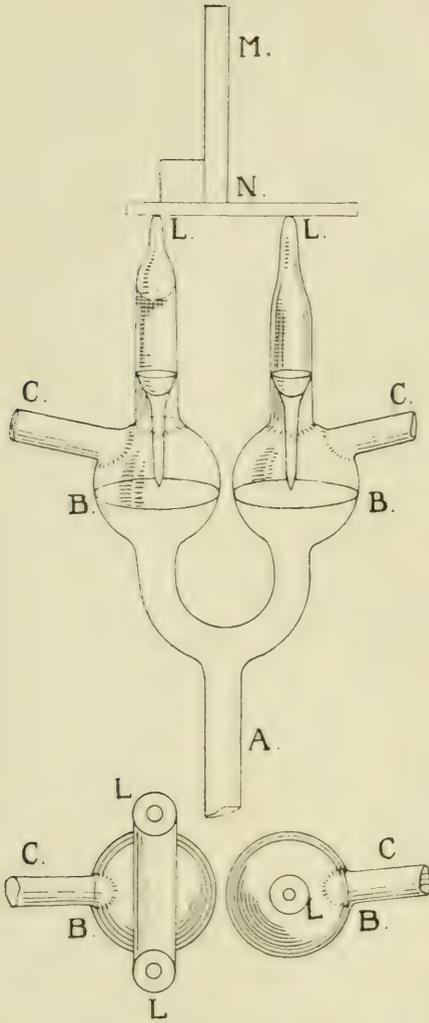


Fig. 1.

the clamp  $H^1$ ) and the screw  $R$ . This point can be very accurately determined, as we can observe the reflected images at the same time with the points and so it is as if we saw twice two points approach each other. If the light of an incandescent lamp  $g$ , concentrated by a lens, was thrown on the manometer through a mirror  $m$ , a great accuracy of adjustment could be reached after some practice, when

<sup>1</sup>) The clamp  $G$  serves for the rough adjustment.

<sup>2</sup>) As it proved necessary to prevent heating of the manometer as much as possible, a thick plate of asbestos  $n$  was adjusted between the incandescent lamp and the manometer; in this plate a glass vessel  $w$  was fastened with a solution of alum for the absorption of the rays of heat.

The manometer  $B$  with barometer tube  $A$  is (see fig. 2) fastened in a groove of a solid board  $P$  by means of Cailletet cement. This board is part of an adjusting table  $S$ , which can rotate round a horizontal axis by means of the screw  $R$ . This axis passes through the points of support of two sets of screws  $Z$ , only one of which is to be seen in the figure 2. The mirror of the manometer has been placed in such a way, that the axis mentioned is parallel to its front and coincides with its middle. The air trap  $V$ , in which the barometer tube ends, is by means of an India rubber tube provided with two clamps  $G$  and  $H$  and connected with a mercury reservoir  $K$ .

The principle, on which this manometer rests, is as follows:

If the barometer tube is filled with Hg as far as in the bulbs  $BB$  and if the pressure is the same in the two legs of the manometer, we can cause the two glass points to just touch the mercury mirrors, which are now in one horizontal plane, by using simultaneously the

the points were simultaneously observed through two magnifying glasses.

The position which the mirror *M* occupies in this adjustment, so the zero position, could be accurately determined by means of a scale and a reading telescope with a cross wire. If now a difference in pressure was brought about e.g. such that the mercury mirror in the left leg fell somewhat and that in the right leg rose somewhat, the adjustment of the two points on the mercury mirrors could be again reached by turning the adjusting table, to which the manometer is fastened, over a small angle to the left by means of the screw *R*, for which at the same time the screw *H* was to be used, as the bulbs *BB* are no perfect spheres, and have not perfectly the same diameter either.

When the glass points are again placed in the required way and the reading glass is again read, it is clear, that we can calculate the difference in level of the mercury mirrors in a simple way from the angle of rotation, when we know the distance between the glass points. If this distance is *l*, the angle of rotation *α*, the difference in height between the two mercury mirrors is:

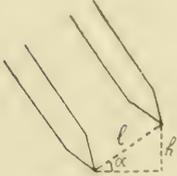


Fig. 3.

$$h = l \sin \alpha.$$

If we represent the deviation observed with the telescope expressed in m.m. *a* and the distance from the scale to the mirror *b*, then  $tg\ 2\ \alpha = \frac{a}{b}$ , for which we may write  $tg\ \alpha = \frac{a}{2b}$  provided *α* be very small.

As further for small angles  $\sin\ \alpha = tg\ \alpha$ , we may write in this case:

$$h = l\ tg\ \alpha = \frac{la}{2b} \dots \dots \dots (1)$$

If the angles are too large for this assumption, we get the following form for *h*:

$$h = \frac{la}{2b} \left( 1 - \frac{3}{2} \frac{a^2}{4b^2} \right) \dots \dots \dots (2)$$

The distance between the glass points was determined by means of a comparator and amounted to 24.66 m.m. = *l*. The distance from the scale to the mirror amounted to 2735 m.m. = *b*.

It now proved that when the deviation *a* was smaller than 100 m.m., formula (1) could be applied, whereas for larger deviations formula (2) appeared to be required.

The accuracy of adjustment, obtained in this arrangement with

Lord RAYLEIGH'S manometer, appeared to amount to 0.1 scale division or to 0.00045 m.m. Hg, whereas with my manometer it amounted to 0.00025 m.m. Hg, as has been said before.

Fig. 4 represents the whole arrangement. *A* is the micromanometer, *B* the automatic mercury air-pump, *C* the manometer of Lord RAYLEIGH and *D* the reading glass with scale and mirror, *a* is a strip of mirror, cut from a sphere. In the focus an incandescent lamp *b* is placed, over which a glass cup has been placed enveloped with filtering paper. A parallel pencil of rays falls through the glass scale *c* and is reflected by the mirror *M* from the manometer into the reading glass *d*.

From this figure the connection of *C* with *A* through the long glass tubes *e* and *f* is also clearly visible. The results obtained by this arrangement are summarized in the following tables.

T A B L E I.  
Na Cl.

Concentration in gr. mol. p. 1000 gr. H <sub>2</sub> O	$p_w - p_s$ in m.m. Hg of 0°.	$p_m$ 1) in m.m. Hg of 0°.	$i = \frac{p_w - p_s}{p_w} \frac{N}{n} = \frac{p_m}{0,08316}$ 2)
0.0441	0.00720	0.163	1.96
0.1073	0.01649	0.151	1.81
0.3823	0.05535	0.1447	1.740
0.6299	0.09125	0.1449	1.742
0.9887	0.14564	0.1473	1.771
2.0476	0.31017	0.1515	1.822
3.3524	0.53442	0.1594	1.917

With the aniline-water manometer the following results had been before obtained.

We see from this that the tables I and II harmonize very well qualitatively; both give a minimum value of *i* for the concentration  $\approx 0.5$  gr. mol.

That there are differences in many cases in the absolute values of *i* is probably due to the uncertainty which exists in applying the temperature correction when working with my manometer. In future

1)  $p_m$  = molecular diminution of vapour tension.

2) 0,08316 = theoretical mol. diminution of vap. tens. at 0°.

## T A B L E II.

## Na Cl.

Concentration in gr. mol. p. 1000 gr. H <sub>2</sub> O	$p_{1c} - p_s$ in m m. Hg of 0°..	$p_m$ in m.m. Hg of 0°.	$i = \frac{p_{1c} - p_s}{p_w} \frac{N}{n} = \frac{p_m}{0,08316}$
0.0591	0.00879	0.149	1.79
0.0643	0.00939	0.146	1.76
0.1077	0.01541	0.143	1.72
0.4527	0.06400	0.141	1.70
0.4976	0.06987	0.141	1.70
1.0808	0.15484	0.143	1.723
1.2521	0.18014	0.144	1.730
1.8228	0.26757	0.147	1.765
2.4927	0.33406	0.153	1.832
4.6362	0.78345	0.169	2.032

it will therefore be advisable to place the manometer in a thermostat. Up to this time the manometer was placed in a glass vessel, through which the water of the aqueduct flowed. If a correction is rendered unnecessary by keeping the manometer at constant temperature, the greater sensitiveness of the aniline-water-manometer will be still more apparent <sup>1)</sup>.

For the comparison of the results of the determinations of the vapour pressure with those obtained in a cryoscopic way, the results of RAOULT <sup>2)</sup>, JONES and GETMAN and mine for NaCl-solutions are placed side by side in the following table.

So RAOULT did not find a minimum in the factor  $i$  in spite of his

<sup>1)</sup> After having read my publication in the Archives Néerlandaises, BATELLI made some measurements with a manometer which differed from mine only in so far, that it was erected in reversed position, in order to make the closure with mercury instead of with oil possible. This change was sufficient, as Prof. CASSUTO, under whose superintendence BATELLI seems to have worked, wrote to me, to omit my name altogether in the publication in the Ann. de Chim. et de Phys. T. XXV 1902, though they used the most essential part of my work viz. a dilute solution of Na OH, Na<sub>2</sub> CO<sub>3</sub> or glass, which causes the aniline to run in a tube of the aqueous solution, and to which the great accuracy is actually due.

<sup>2)</sup> Zeitschr. f. Physik. Chem. 27, 638 (1898).

## T A B L E III.

Na Cl.

Concentration	$i_G$ —RAOULT.	$i_G$ —JONES and GETMAN.	$i_D$ —SMITS.
0.05	1.91	1.89	1.96
0.1	1.86	1.86	1.81
0.5	1.84	1.891	1.74
1.0	1.838	1.906	1.77
2.0		2.007	1.82
3.0		2.190	1.92

$i_G = i$  calculated from the lowering of the freezing point

$i_D =$  » » » » diminution of the vapour tension.

method which seemed so very accurate, though he continued the experiments up to the concentration 1 gr. mol.; JONES and GETMAN, however, found a strongly pronounced minimum lying at the concentration  $\pm 0.1$  gr. mol., whereas the determinations of the vapour tension give a minimum at  $\pm 0.5$  gr. mol.

I have already pointed out in a previous paper<sup>1)</sup>, that only for the case that we have to deal with *exceedingly diluted* solutions the value of  $i$  calculated from the lowering of the freezing point must be in harmony with that calculated from the diminution of the vapour tension.

For the calculation of  $i$  from the lowering of the freezing point the following equation is used:

$$i_G = \Delta T \frac{S}{RT_0^2} \cdot \frac{N}{n} \dots \dots \dots (1)$$

and for the calculation of  $i$  from the diminution of the vapour tension, we applied the equation

$$i_D = \frac{\Delta p}{p_0} \cdot \frac{N}{n} \dots \dots \dots (2)$$

For exceedingly diluted solutions  $i_G = i_D$  or

$$\frac{\Delta p}{p_0} \cdot \frac{N}{n} = \Delta T \frac{S}{RT_0^2} \cdot \frac{N}{n} \dots \dots \dots (3)$$

or

$$\frac{\Delta p}{p_0} = \Delta T \cdot \frac{S}{RT_0^2} \dots \dots \dots (4)$$

<sup>1)</sup> These Proc. III, Febr. 23 1901, p. 507.

For not very dilute solutions this is however no longer the case and as VAN LAAR<sup>1)</sup> found, for them the following relation holds:

$$\log \frac{p_0}{p} = \Delta T \frac{S}{RT_0^2} \cdot \frac{T_0}{T} \cdot \cdot \cdot \cdot \cdot \cdot \quad (5)$$

or

$$\frac{\Delta p}{p_0} + \frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2 = \Delta T \frac{S}{RT_0^2} \cdot \frac{T_0}{T} \cdot \cdot \cdot \cdot \cdot \quad (6)$$

If therefore we wish to compare the results of non-diluted solutions, we can e.g. calculate instead of  $i_G = i_D$  according to (1) and (2) the following values:

$$I_G = \Delta T \frac{S}{RT_0^2} \cdot \frac{T_0}{T} \cdot \frac{N}{n}$$

or

$$I_D = \left[ \frac{\Delta p}{p_0} + \frac{1}{2} \left( \frac{\Delta p}{p_0} \right)^2 \right] \frac{N}{n}$$

which theoretically must have exactly the same value.

I have already shown before<sup>2)</sup>, that the error committed by putting  $i_G = i_D$  instead of  $I_G = I_D$  for not very dilute solutions, is not sensible before we reach the concentration  $\pm 1$  gr.

If we now compare the results obtained by RAOULT, JONES, GETMAN and myself by means of the factor  $I$ , we get the following table:

T A B L E IV.  
Na Cl.

Concentration	$I_G$ — RAOULT.	$I_G$ — JONES and GETMAN.	$I_D$ — SMITS.
0.05	1.91	1.89	1.96
0.10	1.86	1.87	1.81
0.50	1.85	1.904	1.75
1.00	1.86	1.931	1.80
2.00		2.064	1.88
3.00		2.293	2.03

It is obvious that the second column is now qualitatively in concordance with the two following; also the factor  $I$  derived from the observations of RAOULT, gives a minimum, but it is very faint, so faint, that it did not appear in the calculation of  $i_G$  (table III)<sup>3)</sup>.

<sup>1)</sup> Zeitschr. f. physik. Chem. **15**, 457 (1894).

<sup>2)</sup> These Proceedings III, Febr. 23 1901 p. 512.

<sup>3)</sup> This has already been shown by VAN LAAR in a somewhat different way. (Archives Teijler **8** (1903)).

We see further that the differences between the third and the fourth column in this table are about as great as in table IV, so that it is sufficient to calculate  $i_G$  and  $i_D$  for a first investigation of the concordance of the results obtained by different methods.

The investigation of  $\text{NaNO}_3$ -solutions yielded the following result.

T A B L E V.

 $\text{NaNO}_3$ .

Concentration in gr. mol. p. 1000 gr. $\text{H}_2\text{O}$	$p_w - p_s$ in m.m. Hg of $0^\circ$ .	$p_m$ in m.m. Hg of $0^\circ$ .	$i = \frac{p_w - p_s}{p_w} \frac{N}{n} = \frac{p_m}{0.08316}$
0.0515	0.00748	0.443	4.72
0.0901	0.01257	0.439	4.68
0.3385	0.04578	0.4352	4.626
0.8328	0.11042	0.4326	4.594
2.8168	0.33426	0.4176	4.444
4.0544	0.46119	0.41375	4.268
7.3151	0.79056	0.40807	4.300

It follows from this table, that the factor  $i$  decreases continually with  $\text{NaNO}_3$ -solutions.

Also JONES and GETMAN have observed the same course in their determinations of the freezing point, which follows from the following table.

T A B L E VI.

 $\text{NaNO}_3$ .

Concentration.	Molecular freezing point depression	$i$
0.05	3.440	4.85
0.10	3.428	4.843
0.20	3.345	4.798
1.00	3.498	4.719
2.00	3.074	4.653
3.00	2.969	4.596

3. The minimum in  $i$  may be brought about by the formation of hydrates in solution. I showed already before <sup>1)</sup>, how great the influence can be, which the formation of hydrates in solution can exert on the course of the factor  $i$ , specially with regard to not very dilute solutions.

For very small concentrations, however, the number of water molecules is so predominant, that the number of molecules withdrawn from the solution, practically does not bring about any change in the molecular concentration. Towards higher concentrations the increase of the molecular concentration in consequence of the formation of hydrates augments continually, and so it may be assumed, that for a certain concentration it has increased so much, that it has become equal to the diminution of the molecular concentration in consequence of the retrogression of the electrolytic dissociation. If this is the case,  $i$  has reached its smallest value, and will increase towards higher concentration, because the influence of the formation of hydrates prevails more and more over the retrogression of the electrolytic dissociation.

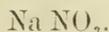
Besides the above mentioned formation of hydrates, we may generally assume auto-complex-formation and hydrolysis, so that probably many electrolytes form a system so intricate, that some time will probably elapse before the desired insight into it will be acquired. Referring here to salts of strong bases and acids I could leave hydrolysis out of account. The auto-complex-formation has not been discussed, because it brings about a diminution of the molecular concentration, and was therefore of no use for the explanation of the phenomenon.

4. Finally I will call attention to the very remarkable fact, that solutions of  $\text{NaNO}_3$ , which qualitatively behave in a very normal way, do not follow the dilution law of OSTWALD, whereas solutions of  $\text{KNO}_3$  follow this law according to my measurements, and as the deviations for  $\text{NaNO}_3$  solutions lie in this direction that  $K$  increases with the concentration as is seen in the following table, this points to an influence as e. g. occurs for  $\text{NaCl}$  solutions, but in a much smaller degree <sup>2)</sup>.

<sup>1)</sup> Archiv. Néerl. (2) 1 (1897).

<sup>2)</sup> That  $\text{KNO}_3$ -solutions harmonize better with the theory than  $\text{NaNO}_3$ -solutions is in accordance with the results of experiments made by ABEGG and BODLANDER (Zeitschr. f. anorg. Chem. 20, 453 (1899)), from which could be derived, that the tendency to complex-formation depends on the degree of the tendency to ionisation, which latter tendency is indicated by the tendency of dissociation. The greater the tendency to ionisation the smaller the tendency to complex-formation. According to WILSMORE (Zeitschr. f. physik. Chem. 35, 318 (1900)) the tension of dissociation is for  $K=3.20$  and for  $\text{Na}=2.82$ , from which would follow, that kalium salts have a slighter tendency to complex-formation than natrium salts.

## T A B L E VII.



From the determinations of the vapour tension at  $0^\circ$   
with Lord RAYLEIGH'S manometer.

Concentration.	Degree of Dissociation $z$	$K = c \frac{z^2}{1-z}$
0.0515	0.72	0.09
0.0901	0.68	0.46
0.3385	0.63	0.35
0.8328	0.59	0.72

From the determinations of the boiling point at  $\pm 100^\circ$ .

0.0462	0.83	0.49
0.0852	0.81	0.28
0.4448	0.72	0.76
0.8630	0.71	1.50

## T A B L E VIII.



From the determinations of the vapour tension at  $0^\circ$  with the  
aniline-water-manometer.

Concentration.	Degree of dissociation $z$	$K = c \frac{z^2}{1-z}$
0.0400	0.81	0.44 <sup>1)</sup>
0.1450	0.58	0.42
0.5997	0.39	0.15
0.9288	0.304	0.42
		average 0.43

From the determinations of the boiling point at  $\pm 100^\circ$ .

0.1000	0.91	0.62 <sup>2)</sup>
0.4991	0.74	1.05
0.7486	0.67	1.02
0.9981	0.651	1.21
		average 1.05

<sup>1)</sup> We must not attach too much importance to the absolute value of  $K$ , as a slight error in the sensibility of the manometer appears in  $K$  greatly magnified.

<sup>2)</sup> By this method we cannot make use of more diluted solutions to test the dilution-law, as the error of the observation has too much influence then. For the concentration 0.1 gr. mol. per 1000 gr.  $\text{H}_2\text{O}$  this influence is already fairly strong. If e.g. for this concentration we had found a rise of the boiling point of  $0.1^\circ$  instead of  $0.099^\circ$ , we should have had  $z = 0.93$  and  $K = 1.23$ .

It is remarkable that the law of dilution proves to apply here up to fairly high concentrations. It would therefore be interesting to carry on the series towards higher concentrations to see where the deviations begin to appear.

That the freezing point method is inferior to the vapour tension method and the boiling point method with a view to accuracy follows also from the fact, that no constant values for  $K$  can be calculated from the observations of LOOMIS, JONES and GETMAN, as appears from the following table.

T A B L E IX.



From the determinations of the freezing point.

Concentration.	Degree of dissociation $\alpha$	$K = c \frac{\alpha^2}{1-\alpha}$
0.05	0.83	0.21
0.10	0.78	0.28
0.20	0.71	0.35
0.40	0.69	0.78
0.50	0.65	0.61
1.00	0.47	0.41

} LOOMIS<sup>1)</sup>.

} JONES and GETMAN.

The fact, however, that BILTZ<sup>2)</sup> obtained concordant results for solutions of caesium nitrate by means of the freezing point method justifies the hope, that when the experiments are made very carefully, also by this method the law of dilution will prove to hold for  $\text{KNO}_3$ -solutions.

I have agreed with Dr. BILTZ that he will examine the behaviour of chlorates, perchlorates and permanganates with regard to the law of dilution and I shall investigate the nitrates.

The above salts manifest little tendency for complex formation and are therefore the most suitable material for the above mentioned purpose.

Febr. 1904, *Amsterdam*.

*Chemical Laboratory of the University.*

<sup>1)</sup> Phys. Rev. **3**, 279 (1896).

<sup>2)</sup> loc. cit.

**Physics.** — “*On the measurement of very low temperatures. VI. Improvements of the protected thermoelements; a battery of standard-thermoelements and its use for thermoelectric determinations of temperature.*”. By H. KAMERLINGH ONNES and C. A. CROMMELIN.

(Communicated in the meeting of November 28, 1903).

§ 1. *Improvements of the protected thermoelements.* Comm. N<sup>o</sup>. 27 II (June '96) contains a description of the apparatus with which at that time the thermoelectric determinations of temperature were made. The measurements for the sake of which these determinations were made are not yet closed, because they have been repeated with constantly improved arrangements. In the mean time the thermoelectric determination of temperature itself has been improved. The experiments of Mr. HOLLMANN<sup>1)</sup> have offered an opportunity for remarks about some of these improvements. Yet up to now a complete description of the modifications made since the appearance of Comm. N<sup>o</sup>. 27 has been deferred. It is now given in the following paper.

Besides the “protected” (comp. Comm. N<sup>o</sup>. 27) observation-elements we still use protected comparison- or standard-elements. We have also retained the construction of both the observation-elements and the comparison- or standard-elements, so that the two “limbs” (the junctures with their protecting-tubes) can be immersed into steam, ice or into some liquefied gas or other to test whether the element is free of current with equal temperatures of the junctures.

For the observation-element we avail ourselves of a combination of constantin and steel to obtain a considerable electromotive force. We found for it with constantin wire furnished by HARTMANN and BRAUN 46 microvolts per degree (0°C.—+100°C.) KLEMENČIČ and CZERMAK<sup>2)</sup> give for constantin-iron 51, CROVA<sup>3)</sup> 63, VAN AUBEL and PAILLOT<sup>4)</sup> 47, H. RUBENS<sup>5)</sup> 53, HOLBORN and WIEN<sup>6)</sup> 56, KLEINER<sup>7)</sup> 58, FUCHS<sup>8)</sup> 54.

1) BAKHUIS ROOZEBOOM. Proc. Vol. 5, p. 283, 1902.

HOLLMANN. Zeitschr. f. Phys. Chem. Bd. 43. 2. p. 129. 1903.

2) KLEMENČIČ and CZERMAK, Wied. Ann. Bd. 50, p. 174. 1893.

3) A. CROVA, C. R. 125, p. 804. 1897.

4) VAN AUBEL and PAILLOT, Arch. d. Sc. phys. et nat. Genève Per. 3 T. 33, p. 148. 1895.

5) H. RUBENS, Zeitschr. f. Instrk. Bd. 18 p. 65. 1898.

6) HOLBORN and WIEN, Wied. Ann. Bd. 59, p. 213. 1896.

7) KLEINER, Arch. d. Sc. phys. et nat. Genève. Per. 3. T. 32, p. 280.

8) FUCHS, Ueber das thermo-electrische Verhalten einiger Nickel-Kupfer-Legierungen, Graz, 1893.

Constantin and steel appeared to satisfy the requirements for thermo-elements laid down in Comm. N<sup>o</sup>. 27. We succeeded in finding wires of which, after they had been treated as described in Comm. N<sup>o</sup>. 27, the potential-differences at a temperature difference of 100° C. amount to no more than 0.5 microvolt along the whole wire and at the extremities over a length from 50 to 60 cm. no more than 0.05 microvolt <sup>1</sup>).

In order to be able to test whether the element is free of current a steel wire has been soldered on to each of the ends of the wire. The junctures of the two steel wires with the copper leads are kept at an equal constant temperature viz. 0° C. Each of these protected junctures constantly kept at 0° C. has its own ice-pot which is mounted insulated from the others (See fig. 1 Pl. I and compare with this figs. 1 and 2 of Pl. I Comm. N<sup>o</sup>. 27).

As to the principal features the arrangement of the limbs like that of the whole element has remained the same as in Comm. N<sup>o</sup>. 27. The constantin wire, which like the German-silver wire might easily be bent in sharp curves and then show disturbing electromotive forces, is again protected by a thickwalled indiarubber tube connected hermetically with the glass protecting-tubes of the limbs. Owing to its elasticity the steel wire did not require this protection; a layer of shellac protects it from rust (for a better protection of this layer it may also be coated with a thinwalled indiarubber tube).

In the limb constantin-steel the constantin-wire (1 mm. thick, 0.25  $\Omega$  resistance per m.) is enclosed in the inner glass tube (see fig. 2 Pl. I and comp. fig. 4 Pl. III Comm. N<sup>o</sup>. 27), the steel wire goes straight between the inner and the outer tube (see fig. 2 Pl. I and comp. fig. 4 Pl. III of Comm. N<sup>o</sup>. 27). Owing to the small conductivity it was not necessary to wind the steel wire round the inner tube (see fig. 4 Pl. III of Comm. N<sup>o</sup>. 27). For the limbs which are always immersed in ice, a firm outer protecting-tube is very desirable with a view to the circumstance that the ice must repeatedly be packed together. Each ice-pot is enclosed in a protecting cone-shaped piece of paste-board soaked in oil of which the lower rim stands in the water on its dish, thus forming an air-jacket round the ice-pot which is closed at the bottom; yet in warm weather it is advisable to pack the ice every five minutes.

Although to simplify the construction of the elements we have

<sup>1</sup>) The defects which were avoided in the treatment described in Comm. N<sup>o</sup>. 27, have later been detected in thermoelements of the Phys. Techn. Reichsanstalt. There the treatment considered has also been applied in following cases. (Cf. Zeitschr. f. Instrk. Bd. 19. p. 249, 1899).

used tubes with two openings (see fig. 6 Pl. I) through which the two wires of the element are drawn, yet in many of these tubes tensions appeared, which proved an impediment to their being operated upon.

Formerly it was very difficult to make a connection between the copperblock (for the meaning of this cf. Comm. N<sup>o</sup>.27) and the protecting-tube, which connection should not only be airtight, but which also must allow of being placed into steam and at low temperatures into different kinds of liquids. This difficulty has been entirely overcome. In N<sup>o</sup>. 27 we have spoken of our intention to try, following the method of CAILLETET, and solder the copper block on to glass which to this end had been platinized. In this we succeeded to perfection. The glass tube is platinized at the end with platinum-chloride in the blow-pipe while care must be taken that it remains perfectly cylindrical, then it is coppered galvanically and tinned over an alcohol flame. Then the thin upright rim turned on to the block, which is also tinned and carefully cleaned, is pushed round the end after which they are soldered together by means of resin as a flux. Then the cap, the juncture seam and the tinned glass together are galvanically platinized and gilt. In this manner an important improvement has been obtained. The indiarubber protecting-ring which made the limb much thicker is removed, the fit is perfectly tight and permanent, the limb may be fastened into almost any apparatus and be immersed into any liquid without the least fear of action on the wires or of shunt-circuits anywhere between the two wires.

Platinizing and gilding are not always necessary. The thermoelement used in the experiments of HOLLMANN i.e. was only tinned, as acetaldehyd does not attack tin. If for one reason or other we do not wish to bring the protected thermoelements into direct contact with a liquid with strong chemical action in which it is immersed, they are enclosed in a separate protecting-tube (see figs. 3 and 4, Pl. I) terminating in a thinwalled copper cap soldered on to it in the way as described above, into which the block of the thermoelement fits exactly, and which cap is covered galvanically with a suitable metal. This auxiliary means was for instance used here in determinations of melting-points of mixtures of chloride and sulphur by Mr. ATEX. Between the limb of the thermoelement and the protecting-tube provided with a platinized and gilt cap, a little pentane was poured to fill up the space.

In addition to the description of Comm. N<sup>o</sup>. 27 we remark that the airtight connection of the outer glass protecting-tubes with the indiarubber protecting-tube has been made by means of indiarubber

foil and indiarubber solution in one of the ways represented in figs. 2, 3 and 5.

For the filling of the tubes we can recommend in general dry hydrogen.

§ 2. *Battery of standard-thermoelements.* At the end of Comm. N<sup>o</sup>. 27 it was remarked that the comparison-thermoelement itself with junctures placed in ice and steam, the electromotive force of the observation-element being expressed in terms of that of the comparison-thermoelement, could be used as a standard. One of the junctures is easily kept at 0° C. when the precautions are taken described in Comm. N<sup>o</sup>. 27 and in this paper § 1. As to the other which is placed in steam we must make sure that in the boiling-apparatus described in Comm. N<sup>o</sup>. 27 the water vapour flows out at a steady rate and we must apply the small correction for the variation of the boiling-point with the barometric height in order to easily reduce the electromotive force to that which would be obtained if this juncture were kept precisely at 100° C. If the metals do not undergo a secular variation, we always have at our disposal a constant electromotive force (although it cannot be reproduced with certainty independent of the special apparatus) which is very appropriate for the calibration of sensitive galvanometers in general, and has moreover the advantage in thermoelectric determinations of temperature that it belongs to the same size as the electromotive force to be measured.

It seems that this idea has later been developed by the Phys. Techn. Reichsanstalt<sup>1)</sup>.

At the time of Comm. N<sup>o</sup>. 27 (June '96) the comparison thermo-element was compared at intervals with a standard-element (then CLARK'S). On the whole it satisfied the requirements better than the CLARK-cell, which had to be replaced repeatedly, while owing to the improvements of the protection of thermoelements we had obtained comparison-thermoelements which could serve unaltered for indefinite time. The favourable experiences made with the German-silver-copper-element in Comm. N<sup>o</sup>. 27 led us to replace the single comparison- or standard-thermoelement by a battery of 3 standard-thermoelements each with its own boiling-apparatus and its own ice-pot, which are mounted insulated. Two of those elements  $P_2$  and  $P_3$  are made of constantin-steel, the third  $Q_2$  is the afore-mentioned German silver-copper-element with a 3 times smaller electromotive force than that of  $P_2$  or  $P_3$ .

<sup>1)</sup> Vgl. Zeitschr. f. Instrk. Bd. 17, p. 174, 1897.

Idem Bd. 18, p. 183, 1898.

Idem Bd. 22, p. 149, 1902.

Idem Bd. 23, p. 174, 1903.

By means of an elements-switch of which the arrangement may be seen without further description from Pl. I fig. 7 and Pl. II, we can switch the single elements or combinations of them in series or in opposition and obtain electromotive forces in the ratios of 1, 2, 3, 4, 5, 6, 7 which by the central commutator of the elements-switch are connected to the galvanometer wires  $G$  in a positive or negative sense. The elements-switch has been made of galvanoplastic copper (mounted on ebonite) and packed in a case with cottonwool so that there electromotive forces are excluded.

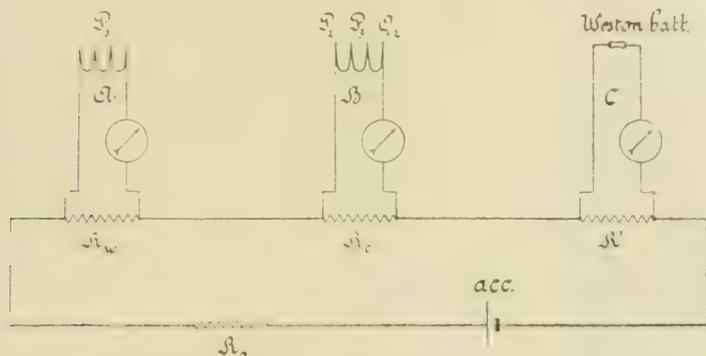
The electromotive forces mentioned cover at intervals of about 30 degs more than the whole range of temperatures below  $0^{\circ}$  C. Therefore in the measurement of a temperature we can each time use a very near combination of standard-thermoelements for comparison.

§ 3. *Determinations of the electromotive forces of the observation-element.* In Comm. N<sup>o</sup>. 27 the observation- and the comparison-element were compared by means of the deflections which they produced successively on the same galvanometer. This deflection-method must always be applied whenever the determinations must be made quickly. For these determinations of the deflection the string-galvanometer of EINTHOVEN<sup>1)</sup> which owing to its sensibility and independence of magnetic disturbances would for the rest be probably also very suitable for thermoelectric determinations, would have the advantage above other galvanometers that the indications are instantaneous. An opportunity to test this instrument has not yet presented itself.

In determinations, however, where we especially want to observe fluctuations of the electromotive force about an almost constant value a compensation-method offers large advantages. In order to avail ourselves of the advantages offered by the circumstance that the electromotive forces to be compared are approximately equal, the switching in opposition of the observation- and the comparison-element was rendered possible in Comm. N<sup>o</sup>. 27, where the battery of the standard-elements of the nearest electromotive force would then be used. To the arrangement of Comm. N<sup>o</sup>. 27 for measurements of deflections an arrangement has been added which allows of a determination of the electromotive force of the observation-element at perfect compensation by means of a zero-method. Thus the comparison of the standard-element with the CLARK-cell of the arrangements of Comm. N<sup>o</sup>. 27 by means of the deflection-method is left out. In this case the element must give a very small but

<sup>1)</sup> Proc. 1903—1904 p. 107.

perceptible current while its resistance, owing to the variations which it undergoes, must always be determined separately. The connections which instead of this are added to that of Comm. N<sup>o</sup>. 27 are in principle the potentiometer-arrangement and have been drawn diagrammatically in the annexed figure <sup>1</sup>).



In the circuit of an accumulator (with a negligible resistance) three resistance-boxes  $R_a$ ,  $R_w$ ,  $R_c$  and a fixed resistance  $R'$  are introduced, of which the first serves to regulate the resistance in the whole circuit, the second and third serve as shunts for two circuits  $A$  and  $B$  in which the observation-element and the battery of comparison-elements are inserted, while the third, a resistance of  $8000 \Omega$  tested at the Phys. Techn. Reichsanstalt serves as a shunt for the circuit  $C$ , in which is inserted a battery of WESTON-elements. These side circuits may be connected to the galvanometer, each by means of its own commutator with mercury contacts (as described in Comm. N<sup>o</sup>. 27 see pl. V) and be commutated in order to read in how far we have attained the desired zero-adjustment by regulation of the different resistances and to apply a correction for the deflection which might have remained.

The principal resistance-boxes are adjusted by means of plugs like the auxiliary boxes arranged in parallel for the finer adjustment. This is preferable to an adjustment with a slide-wire where also small differences remain <sup>2</sup>). As the  $R_a$ ,  $R_w$  and  $R_c$  are known approximately beforehand, (with an adjustment at  $-116^\circ \text{C}$ . about  $7290 \Omega$ ,  $40 \Omega$  and  $40 \Omega$  respectively) the current given by the WESTON-elements will always be very small. In order to make it still less

<sup>1</sup>) Cf. for instance JAEGER, Die Normalelemente, p. 100.

DEWAR and FLEMING, Phil. Mag. (5), 40, 95. 1895.

<sup>2</sup>) Cf. LEHFELDT, Phil. Mag. Ser. 6 Vol. 5. p. 668. 1903.

disadvantageous five of those elements, in order to obtain an equal distribution of the current each with a series-resistance of 5000  $\Omega$ , are connected parallel to each other. Finally, when the adjustment is obtained, the battery which has served in the regulation is replaced by altering a plug in the commutator, by a battery arranged in the same way, which serves for the measurements.

The peculiarity of this arrangement is that we can make immediately after each other all the readings required for the measurements by handling the commutator-boards (comp. successively Pl. V Comm. N<sup>o</sup>. 27) and without making other contacts than those of mercury; this would be impossible without the commutators and the current-reversers with mercury-contacts. This again reveals the great advantages which these apparatus offer for similar measurements. It seems, however, that little attention has been paid to them.

The whole arrangement with 6 current-reversers 1, 2, 3, 4, 5, 6 and 4 commutators *A*, *B*, *C*, *D* for both deflection- and zero-method as it has become now may be easily seen on Pl. II. The current-reversers and commutators with mercury-contacts have been indicated by three and four parallel lines respectively.

1 serves to connect one of the two galvanometers, that of HARTMANN and BRAUN, described in Comm. N<sup>o</sup>. 27 or a magnetically protected galvanometer of DU BOIS and RUBENS.

2 and 4 to switch the galvanometer on to one of the three branches *A*, *B*, *C*,

3 to switch the battery of comparison-elements on to the branch *A* or on to *B*,

5 to introduce the observation-element and the comparison-battery separately or in series or in opposition (cf. 3),

6 to introduce either the observation-element or the comparison-elements.

*A*, *B* and *C* make and reverse the connection of the three circuits with the galvanometer, *D* reverses the accumulator. The commutators and the current-reversers, like the WESTON-battery have been packed in cottonwool, placed together in large cases. Only the tubes where the contact of the mercury is made by handling the commutator-board (see Pl. V Comm. N<sup>o</sup>. 27) project beyond it.

**Physics.** — “Contributions to the knowledge of VAN DER WAAALS’  $\psi$ -surface. VIII. The  $\psi$ -surface in the neighbourhood of a binary mixture which behaves as a pure substance.” By Dr. J. E. VERSCHAFFELT. Supplement n<sup>o</sup>. 7 to the Communications from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of October 31, 1903).

*General part.*

Distillation of a mixture without its composition being altered, and reversely also condensation of a mixture by decrease of volume, without variation of pressure, quite as a pure substance, can only occur at one special temperature. Experiments of KUENEN<sup>1)</sup> have shown for the first time that this phenomenon may be observed in the neighbourhood of the plaitpoint of the mixture; this circumstance has been theoretically investigated and explained by VAN DER WAAALS<sup>2)</sup>.

If a mixture behaves as a pure substance just at the plaitpoint temperature the critical point of the homogeneous mixture, the critical point of contact and the plaitpoint coincide at a same point which may therefore properly be called the critical point of the special mixture and of which I shall represent the elements, as for a simple substance, by  $T'_k$ ,  $p_k$  and  $v_k$ .

Then according to VAN DER WAAALS<sup>3)</sup> we have at the plaitpoint  $\left(\frac{\partial p}{\partial v}\right)_{T_k} = 0$ . Hence the isothermals of two neighbouring mixtures at the same temperature must intersect in pairs, so that the system of isothermals of the mixtures at the critical temperature of the special mixture must agree with fig. 16 of my paper in these Proc. Oct. 25 1902 p. 345. In the annexed figure a similar system of isothermals is drawn according to observations of QUINT<sup>4)</sup> with mixtures of hydrochloric acid and ethane.

Although the special mixture behaves as a simple substance at the critical point, yet it does not follow from this that its border curve on the  $p, v, t$  diagram may be found in the same way as for a simple substance, i. e. by making use of the theorem of MAXWELL-CLAUSIUS. For just below the critical temperature the pressure no longer remains unchanged during the condensation and the experimental isothermal is no longer perfectly parallel with the  $v$ -axis,

1) Phil. Mag., 40, 173—194, 1895. *Comm. phys. lab. Leiden*, n<sup>o</sup>. 16.

2) *Arch. Néerl.*, 30, 266, 1896.

3) *Contin.* II p. 116.

4) Thesis for the doctorate, Amsterdam 1900.

though the variation of pressure is vanishingly small. Consequently the system of isothermals satisfies the law of corresponding states, but the border curve does not necessarily do so. Hence we shall see that for the border curve this is only the case to a first and a second approximation.

*The  $\psi$ -surface.* I shall represent by  $x_k$  the composition of the mixture which behaves as a simple substance. In the neighbourhood of the critical point the system of isothermals of this mixture may be represented by the equations (2) and (2') of my paper in these proc. Oct. 25 1902 p. 321; for the rest all the considerations of sections 2 and 3 of the same paper are directly applicable, except that  $x - x_k$  must everywhere be substituted for  $x$ , and hence also  $x_{Tk} - x_k$  for  $x_{Tk}$ . Thus we find back, for the system of isothermals of the mixtures at a temperature which differs little from  $T_k$ , the equations (18) and (18'), where  $x - x_{Tk}$  is vanishingly small, but not  $x$  and  $x_{Tk}$  separately; from the circumstance that at the critical point  $\left(\frac{\partial p}{\partial v}\right)_v = 0$ , it also follows that  $m_{01} = 0$ ; and because  $m_{01} = p_k \beta - k_{01} T_k \alpha$  we must have:

$$\frac{\beta}{\alpha} = k_{01} \frac{T_k}{p_k} = \left(\frac{\partial p}{\partial T}\right)_k = 7.3 \dots \dots \dots (1)$$

Finally we may remark that whereas in fig. 16 (l. c.) the dotted line which, agreeing with  $x < 0$ , had no physical meaning, this line can really exist here, since  $x < x_k$  may as well be imagined as  $x > x_k$ .

The equation of the  $\psi$ -surface may now be written in this case:

$$\begin{aligned} \psi = & - m_0 (v - v_{Tk}) - \frac{1}{2} m_1 (v - v_{Tk})^2 - \frac{1}{3} m_2 (v - v_{Tk})^3 - \frac{1}{4} m_3 (v - v_{Tk})^4 \dots \\ & + RT x_k (1 - x_k) \left[ \frac{1}{1.2} \frac{(x - x_k)^2}{x_k^2 (1 - x_k)^2} + \frac{2x_k - 1}{2.3} \frac{(x - x_k)^3}{x_k^3 (1 - x_k)^3} + \right. \\ & \left. + \frac{3x_k^2 - 3x_k + 1}{3.4} \frac{(x - x_k)^4}{x_k^4 (1 - x_k)^4} + \dots \right], \dots \dots \dots (2) \end{aligned}$$

where again a linear function of  $x$  is omitted, while  $m_{00} = p_{Tk}$ , and further  $m_{01}$ ,  $m_{10}$  and  $m_{20}$  may be put equal to zero.

*The border curve at a temperature  $T$ .* In the same way as before<sup>1)</sup> I find, putting

$$\begin{aligned} \frac{1}{2} (v_2 + v_1) - v_{Tk} &= \Phi, & \frac{1}{2} (v_2 - v_1) &= \varphi \\ \frac{1}{2} (x_2 + x_1) - x_{Tk} &= \Xi, & \frac{1}{2} (x_2 - x_1) &= \xi, \end{aligned}$$

$v_1$   $v_2$   $x_1$   $x_2$  representing the molecular volumes and the molecular compositions of the coexisting phases, that

<sup>1)</sup> These Proc. V, Oct. 25 1902, p. 330.

$$\varphi^2 = -\frac{m_{11}}{m_{30}} \Xi \dots \dots \dots (3)$$

$$\Phi = -\frac{1}{m_{30}} \frac{m_{11} \left( 2m_{02} m_{30} - \frac{1}{3} m_{11} m_{21} \right) + \frac{2RT}{x_k(1-x_k)} \left( \frac{1}{3} m_{21} m_{30} - \frac{2}{5} m_{11} m_{40} \right)}{m_{11}^2 + \frac{2RT m_{30}}{x_k(1-x_k)}} \Xi \quad (4)$$

$$\frac{\varphi}{\Xi} = 4 m_{30}^2 \frac{m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} \frac{m_{11}^2 m_{40}}{m_{30}^2}}{m_{11}^2 + \frac{2RT m_{30}}{x_k(1-x_k)}} \Xi \dots \dots \dots (5)$$

$$p_1 - pTk = \left( m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} m_{11}^2 \frac{m_{40}}{m_{30}^2} \right) \Xi^2 \dots \dots \dots (6)$$

The relations (2) and (5) are the same as I have found before<sup>2)</sup> for the special case  $m_{01} = 0$ , on the edge of the  $\Psi$ -surface, while the expression for  $\Phi$  becomes the same when we put  $x_k = 0$  or  $x_k = 1$ . I also find again for the border curve on the  $p, v$  diagram of the mixtures at the temperature  $T$  to the first approximation the same parabola of the fourth degree:

$$p - pTk = \frac{m_{30}^2}{m_{11}^2} \left( m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} \frac{m_{11}^2 m_{40}}{m_{30}^2} \right) (v - vTk)^4 \dots (7)$$

The plaitpoint, i. e. the apex of this parabola, coincides to the first approximation with the point  $pTk, vTk, xTk$ . According as the factor between brackets is positive or negative this parabola is turned upwards or downwards; in the first case the special mixture has a minimum vapour tension, in the second a maximum vapour tension.

*The isobars.* If in equation (18) l. c. p. 327 we consider  $x$  and  $v$  as two variable quantities depending on each other and  $p$  as a parameter, this equation represents the projection of the system of isobars on the  $x, v$ -surface. If  $m_{01}$  were not zero this system would resemble a system of isothermals with the point  $xTk, vTk$

1) Of all the coefficients  $m$  which occur here I have formerly given the expressions in the  $k$ 's and  $\alpha$  and  $\beta$ , except of  $m_{02}$ , for which the expression follows here:  $m_{02} = \beta' p_k + k_{01} \alpha (a - \beta) T_k + k_{02} \alpha^2 T_k^2 + k_{11} \alpha (a - \beta) v_k T_k - k_{01} a' T_k$  or reduced:

$$= p_k [\beta + \alpha (a - \beta) v_{01} + \frac{1}{2} \alpha^2 v_{02} + \alpha (a - \beta) v_{11} - a' v_{01}].$$

2) These Proc. V, Oct. 25, 1902, p. 329.

as critical point<sup>1)</sup>. Here it consists, in the neighbourhood of that same point, in a double system of curves of hyperbolic shape, as may be seen in the annexed figure, separated by two curves, of which the equation is obtained by putting  $p = p_{Tk}$ . To the first approximation the system of isobars is represented by the equation

$$m_{02} (x - x_{Tk})^2 + m_{11} (x - x_{Tk}) (v - v_{Tk}) = p - p_{Tk}, \dots \quad (8)$$

which represents hyperbolae, of which the one asymptote is:

$$x - x_{Tk} = - \frac{m_{11}}{m_{02}} (v - v_{Tk}) \dots \dots \dots \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} (9)$$

while the second,  $x - x_{Tk} = 0$ , may be written to the second approximation

$$x - x_{Tk} = - \frac{m_{30}}{m_{11}} (v - v_{Tk})^2 \dots \dots \dots$$

*The connodal line.* In order to find the projection of the connodal line on the  $x, v$ -surface we eliminate  $p - p_{Tk}$  between the equation of the isobar and that of the border curve; we then find to the first approximation

$$(x - x_{Tk}) = - \frac{m_{30}}{m_{11}} (v - v_{Tk})^2 \dots \dots \dots (10)$$

The critical point of contact, the apex of this hyperbola, coincides, like the plaitpoint, to the first approximation with the point  $x_{Tk}, v_{Tk}, p_{Tk}$ .

*The border curve for a mixture x.* If in the equation (8) we consider  $x$  as constant and  $T$ , hence  $x_{Tk}$  and  $v_{Tk}$  as variable, and if finally we make use of the equation of state of the mixture (equation (13) l.c. p. 325) to express  $T$  in  $p$  and  $v$ , we obtain the

<sup>1)</sup> The systems of isobars may then be written in the form:

$$x = n_0 + n_1 (v - v_{Tk}) + n_2 (v - v_{Tk})^2 + \dots$$

where the  $n$ 's are still functions of  $p$ , for instance:

$$n = n_{00} + n_{01} (p - p_{Tk}) + n_{02} (p - p_{Tk})^2 + \dots$$

If the  $n$ 's are expressed in the  $m$ 's, we find:

$$\begin{aligned} n_{00} &= x_{Tk}, \quad n_{01} = \frac{1}{m_{01}}, \quad n_{02} = - \frac{m_{02}}{m_{01}^3}, \dots, \quad n_{10} = 0, \quad n_{11} = - \frac{m_{11}}{m_{01}^2}, \\ n_{12} &= 3 \frac{m_{02} m_{11}}{m_{01}^4} - \frac{m_{12}}{m_{01}^2}, \dots, \quad n_{20} = 0, \quad n_{21} = \frac{m_{11}^2}{m_{01}^3} - \frac{m_{21}}{m_{01}^2}, \dots, \\ n_{30} &= - \frac{m_{30}}{m_{01}}, \dots, \quad n_{40} = \frac{m_{11} m_{30}}{m_{01}^2} - \frac{m_{40}}{m_{01}}, \text{ etc.} \end{aligned}$$

border curve of the mixture  $x$  in the  $\rho$ ,  $c$ ,  $T$  diagram. To the first approximation its equation is:

$$p - p_{xk} = - \frac{k_{01} k_{30}}{k_{11}} (v - v_{xk})^2, \quad . . . . . (11)$$

as for a simple substance<sup>1)</sup>. Hence to the first approximation the border curve satisfies the law of corresponding states.

That the border curve, apart from the deviations existing already in pure substances does not altogether satisfy the law of corresponding states, has a double cause. It is not only for mixtures which differ little from the special mixture  $x_k$  that the experimental isothermal shows a slight slope, but this is even the case for the mixture  $x_k$  itself; only at the plaitpoint temperature it is perfectly horizontal so that already for the mixture  $x_k$  the border curve must deviate from the law of corresponding states. If as before<sup>1)</sup> we develop the equation of the experimental isothermal:

$$\frac{v - v_{Tk}}{x - x_{Tk}} = \frac{\Phi}{\Xi} = \frac{g}{\xi},$$

we find:

$$p - p_{Tk} = \left( m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} \frac{m_{11}^2 m_{40}}{m_{30}^2} \right) (x - x_{Tk})^2 - 8m_{30}^2 \frac{\left( m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} \frac{m_{11}^2 m_{40}}{m_{30}^2} \right)^2}{m_{11}^2 + \frac{2RTm_{30}}{x_k(1-x_k)}} (v - v_{Tk})(x - x_{Tk})^2 + . (12)$$

and hence, for  $x = x_k$ ,

$$p = p_k + k_{11}(T - T_k) - 8m_{30}^2 \frac{\left( m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} + \frac{1}{5} \frac{m_{11}^2 m_{40}}{m_{30}^2} \right)^2}{m_{11}^2 + \frac{2RTm_{30}}{x_k(1-x_k)}} (v - v_k) \frac{(T - T_k)^2}{\alpha^2 T_k^2} + (13)$$

only for  $x_k = 0$  or  $1$ , that is to say for the pure substances, the third term is left out — and in the same way all the terms which contain  $v - v_k$ .

If now by elimination of  $T - T_k$  between the equation of state of the mixture  $x_k$  (equation (2), l. c. p. 323) and the experimental isothermal (10), we search for the border curve for that special mixture, we see that the slope of the experimental isothermal only influences the third term — viz. with  $(v - v_k)^4$  — in the development (11) of the border curve, so that this border curve only to a third approximation shows a deviation from the law of corresponding

<sup>1)</sup> These Proc. V, Oct. 25, 1902, p. 336.

states. Also for a neighbouring mixture this deviation is only perceptible in third approximation, while for mixtures with a small composition, i. e. on the edge of the  $\psi$ -surface, it exists already in second approximation.

The cause of this smaller deviation in mixtures near the special mixture must be looked for in the circumstance that those mixtures in all their qualities deviate only in second approximation from a single substance; thus we deduce from equation (11) that the critical points: plaitpoint, critical point of contact, critical point of the homogeneous mixture and point of maximum coexistence pressure, differ only in second approximation, so that the four curves (in the space with  $p$ ,  $v$  and  $T$  as coordinates), which connect these critical points of all mixtures touch each other at the critical point of the special mixture, which in general is not the case at the two critical points of the pure components.

*Application to mixtures of hydrochloric acid and ethane.*

The experiments of KUENEN with mixtures of ethane and nitrous oxide, the first where the existence was shown of a mixture that in its critical phenomena agrees with a simple substance, does not allow us to form a complete image of the conduct of neighbouring mixtures. Besides, his investigations were only aimed at the discovery of the second kind of retrograde condensation, and the existence of that special mixture was a new discovery, and not the object of the investigation. Suitable data for our purpose are given by the measurements of QUINT on mixtures of hydrochloric acid and ethane; according to QUINT the composition of the mixture which behaves as a simple substance is  $x_k = 0.44$ , i. e. 0.44 gram molecules ethane and 0.56 gram molecules hydrogen chloride. Mixtures behaving as a pure substance have also been observed bij CAUBET<sup>1)</sup> in his experiments with  $\text{CH}_3\text{Cl}$  and  $\text{SO}_2$ ; as CAUBET however investigated only two mixtures of this binary system, his data are insufficient for our purpose.

In order to proceed with the mixtures investigated by QUINT in the way indicated by KAMERLINGH ONNES, we must determine in the first place the critical elements of the homogeneous mixture  $T'_{xk}$ ,  $p'_{xk}$ ,  $v'_{xk}$ . Instead, however of drawing, the  $\log pv$ ,  $\log v$  or  $\frac{pv}{T}$ ,  $\log p$  diagrams it was sufficient, as in the case of my former investigations<sup>2)</sup> of the

<sup>1)</sup> Liquéfaction des mélanges gazeux, Paris, 1900.

<sup>2)</sup> Arch. Néerl., (2), 5, 644, 1900.

mixtures of carbon dioxide and hydrogen to use the  $\log p$ ,  $\log v$  diagrams, as I found that not only the logarithmical diagrams of the pure substances but also those of the four mixtures investigated could be made to coincide with the logarithmical diagram of carbon dioxide by shifting them parallel to each other.

Unfortunately QUINT made only few observations in the neighbourhood of the critical point, a circumstance which rendered this investigation rather difficult. For it is by means of those very parts situated in the neighbourhood of the point of inflection that the superimposing of the diagrams may be obtained in the most accurate way, while in the area of the larger volumes a shifting within rather wide limits does not cause a perceptible deviation of the superimposed diagrams. Especially the want of observations in the neighbourhood of the critical point in the case of hydrochloric acid is to be regretted because the difference between the critical point given by QUINT and that found by shifting is much larger than we should expect, the diagrams covering each other in a satisfactory way. The more so because, when for ethane and carbon dioxide the diagrams are made covering each other in the observed area the critical points too coincide.

Here follow the values found, for the different mixtures, as elements of the critical point of the homogeneous mixture:

$x =$ (pure HCl)	0,1318	0,4035	0,6167	0,7141	(1 pure $C_2H_6$ )	
$xk =$	42°,5	30°,0	26°,4	25°,8		
$p_{xk} =$	77,3 atm.	65,5	58,6	55,7		
$v_{xk} =$	0,00429	0,00190	0,00543	0,00570		
$t_{xpl} =$	51°,3	43°,1	30°,53	27°,25	27°,37	31°,88
$p_{xpl} =$	84,13 atm.	77,51	65,42	54,30	56,84	48,94
$v_{xpl} =$	0,00380	0,00420	0,00471	0,00540	5,00576	0,00652
$C_4 =$	3,48	3,46	3,45	0,45		3,50

In order to make a comparison I have written in this table the plaitpoint elements of the mixtures as observed by QUINT, and in the last line the values of the expression  $C_4 = \frac{RT_{xk}}{p_{xk} v_{xk}}$  which here are about the same for all the mixtures, especially in the neighbourhood of the special mixture. By means of QUINT's data we find however, for HCl, the much larger number  $C_4 = 3,71$ ; this deviation evidently must be brought in connection with the other one I mentioned before.

If we draw the  $t_{xk}$  and  $t_{xpl}$  as ordinates and  $x$  as abscis we obtain two curves which obviously touch each other at one point; it is difficult, however, to define this point of contact precisely. If the same is done with  $p_{xk}$  and  $p_{xpl}$ , the determination of the point of contact of the two curves is even less certain, owing to the circumstance that, according to the table above, for  $x = 0,4035 = p_{xk} > p_{xpl}$ , which surely follows from the inaccuracy of the method. And the deduction of this point of contact from a graphical representation of the  $v_{xk}$  and  $v_{xpl}$  is quite impossible because these volumes are known by no means with sufficient accuracy.

Therefore it seems to me that the best method is that of QUINT who deduced the composition of the special mixture from the shape of the plaitpoint curve by searching on this curve the point where the bordercurve, which terminates at that point, touches the plaitpoint curve. That point may be determined fairly accurately: we find for its coordinates  $t_k = 29^{\circ},0$  and  $v_k = 63,8$  atms., whence again  $x_k = 0,44$  and  $v_k = 0,00500$ .

By means of the graphical representations of the  $t_{xk}$ ,  $p_{xk}$  and  $v_{xk}$  I find in the neighbourhood of  $x_k = 0,44$ ,  $\frac{dT_{xk}}{dx} = -20$ ,  $\frac{dp_{xk}}{dx} = -30$  and  $\frac{dv_{xk}}{dx} = 0,0020$ ; hence  $\alpha = -0,07$   $\beta = +0,50$  and  $\gamma = 0,40$ , so that the relations  $\gamma = \alpha - \beta$  in  $\frac{\beta}{\alpha} = 7,3$  are confirmed in a satisfactory way.

By means of QUINT's observations, by inter- or extrapolation, partly also by using the law of corresponding states and the values of  $t_{xk}$ ,  $p_{xk}$ ,  $v_{xk}$  found above, I have drawn the isothermals for the 6  $x$ -values considered, at the critical temperature  $29^{\circ},0$  C. of the special mixture  $x = 0,44$ . Those isothermals are represented in the annexed figure, which thus shows the  $p$ - $v$ -diagram of the mixtures at the temperature  $29^{\circ},0$  C. The dot-dash line is the critical  $x = 0,44$  with the critical point in  $C$ . The isothermal  $x = 0,40$  is a dash line in the unstable part; owing to their small curvature the experimental isothermals are represented by straight lines. The border curve is a complete line like the observable parts of the isothermals.

Under the  $p$ ,  $v$ -diagram I have represented the projection on the  $v$ ,  $x$ -surface. The critical isobar (63.8 atms.) is represented by a dot-dash line; some other isobars are drawn, like the projection of the connodal line (also projection of the afore-mentioned border curve), while the isobars in the unstable part, i. e. within the projection, are dotted. The temperature  $29^{\circ}$  being lower than the critical temperature

of pure ethane ( $31^{\circ}.88$ ), the connodal line consists of another part, which I have not drawn, however, in order not to make the figure uselessly intricate. This second piece should have its apex, the critical point of contact, at about  $x_{Tk} = 0.92$ , and  $v_{Tk} = 0.0063$ , and would intersect the axis  $x = 1$  at  $v = 0.00472$  and  $v = 0.01031$ .

To this second piece of the connodal a second border curve corresponds which would begin at a height  $p = 46.1$  (maximum tension of ethane at  $29^{\circ}.0$  C.) and terminate at the plaitpoint  $p_{Tpl} = 51.2$ ,  $v_{Tpl} = 0.0063$ . But this border curve too I have omitted like the isothermal of pure ethane.

At the lower part of the figure it may be seen that the isobars in the neighbourhood of the critical point  $C$ , indeed to the first approximation, are hyperbolae of which one of the asymptotes, which agree with the critical pressure, is parallel to the  $v$ -axis, the other cuts this axis at a given angle. To the second approximation the first asymptote is a parabola which coincides with the projection of the connodal line.

It were useless to investigate whether indeed the border curve is of the fourth degree and the connodal of the second degree; for this the data are not numerous enough and the drawing not sufficiently accurate. But it is obvious why the border curve should be of a higher order than the connodal. The  $p, v, x$ -surface, of which the projections on the surfaces  $p, v$  and  $x, v$  are shown in the fig., is in the neighbourhood of the critical point a saddle-shaped surface, which at the upper part of the figure is seen parallel to the tangent surface at the point  $C$ . The isothermals of the mixtures  $x = 0$ ,  $x = 0.14$  and  $x = 0.40$  are situated on the slope turned towards us; the latter over a fairly extensive range (of large volumes to about  $x = 0.006$ ) forms nearly the border of the surface; the critical isothermal lies just beyond that border, but becomes visible at  $C$  and remains visible for small volumes. The isothermals  $x = 0.62$ ,  $x = 0.71$  and  $x = 1$  occur on the back of the  $p, v, x$ -surface, yet for small volumes they become visible. The parabola:

$$p - p_{Tk} = -\frac{1}{4} \frac{m_{01}^2}{m_{02}} (v - v_{Tk})^2,$$

which envelops the isothermals in the neighbourhood of the point  $C$  (l. c. p. 344 and fig. 16) is the apparent outline of the surface in that neighbourhood.

The lower part of the figure represent the surface seen from above; the isobars are there level-curves. The critical isobar forms a loop which agrees with the described shape of the surface. A section of a horizontal surface situated a little higher consists of two pieces,

of which one, lying within the loop is closed. Within the loop therefore, the surface shows an elevation of which the top almost agrees with  $x = 0.40$ ,  $v = 0.06$ ,  $p = 63.9$ . For higher horizontal surfaces the section consists of one branch only. For horizontal surfaces corresponding to  $p < 63.8$  atm., the sections also consist in one branch which surrounds the critical loop.

From  $x = 0$  the bordereurve occurs on the front of the  $p, v, x$ -surface, but reaches the border almost at the volume 0.008, then occurs on the back where it remains until the point  $C$ , and returns to the front. At the point  $C$  the osculation plane to the border curve, at the same time the tangent plane to the surface, is horizontal; the projection on the  $x, v$ -plane shows the border curve more and more in its true shape the more we approach the point  $C$ ; whereas in the upper projection that border curve is seen more and more in an oblique direction and finally in a tangent one, so that it must appear flattened, which accounts for the higher order of the border curve in that projection.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday March 19, 1904.

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Afdeling van Zaterdag 19 Maart 1904, Dl. XII).

C O N T E N T S.

- A. F. HOLLEMAN: "The nitration of Benzene Fluoride", p. 659.  
JAN RUTTEN: "Description of an apparatus for regulating the pressure when distilling under reduced pressure." (Communicated by Prof. S. HOOGWERFF), p. 665.  
H. KAMERLINGH ONNES: "Methods and apparatus in the cryogenic laboratory. VI. The methylchloride circulation", p. 668. (With 2 plates).  
H. KAMERLINGH ONNES and H. HAPPEL: "The representation of the continuity of the liquid and gaseous conditions on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of GIBBS", p. 678. (With 4 plates).  
P. VAN ROMBURGH: "On Oeimehe." (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 700.  
P. VAN ROMBURGH: "Additive compounds of s. trinitrobenzene." (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 702.  
E. VERSCHAFFELT: "Determination of the action of poisons on plants." (Communicated by Prof. C. A. LOBRY DE BRUYN and Prof. HUGO DE VRIES), p. 703.  
W. EINTHOVEN: "On some applications of the string-galvanometer". p. 707.  
A. F. HOLLEMAN: "Action of hydrogen peroxyde on diketones 1,2 and on  $\alpha$ -ketonic acids", p. 715  
L. E. J. BROUWER: "On a decomposition of a continuous motion about a fixed point  $O$  of  $S_1$  into two continuous motions about  $O$  of  $S_2$ 's." (Communicated by Prof. D. J. KORTEWEG), p. 716  
C. A. LOBRY DE BRUYN and L. K. WOLFF: "Can the presence of the molecules in solutions be proved by application of the optical method of TYNDALL?" p. 735.  
J. J. BLANKSMA: "On the substitution of the core of Benzene." (Communicated by Prof. C. A. LOBRY DE BRUYN and A. F. HOLLEMAN), p. 735.

The following papers were read:

**Chemistry.** — "*The Nitration of Benzene Fluoride.*" By Prof.  
A. F. HOLLEMAN.

(Communicated in the meeting of February 27, 1904).

DR. BEEKMAN who made some communications in his dissertation as to the above nitration came, although his experiments remained unfinished, to the conclusion that in this case the isomeric mononitrocompounds are formed in quite a different proportion as in the nitration of the other halogen benzenes. As it appeared to me very

important to further confirm this statement and as Dr. BEEKMAN could not undertake this himself, I have studied this subject once more and now communicate the results obtained.

The difficulty which presented itself was that we were unable to obtain benzene orthonitrofluoride so that it was impossible to apply the methods which, in the case of the products of nitration of the other halogen benzenes, lead to the knowledge of the proportion in which the isomers are formed. Two observations by Dr. BEEKMAN furnished us, however, with a key to find the said proportion. These were: 1. the very ready transformation of benzene *p*-nitrofluoride with sodium methoxide into the corresponding anisol; 2. the further nitration of the benzene orthonitrofluoride present in the nitrating mixture to benzene dinitrofluoride ( $\text{Fl} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4$ ) which compound has been obtained by Dr. BEEKMAN in a pure condition.

I convinced myself in the first place of the quantitative course of the transformation of benzene *p*-nitrofluoride with  $\text{NaOCH}_3$ .

1.8347 grams of *p*- $\text{NO}_2$   $\text{C}_6\text{H}_4$ .  $\text{Fl} = 13.01$  millimols. were dissolved in a very little pure methyl alcohol, an equivalent quantity of sodium methoxide dissolved in methyl alcohol to the concentration of 0.75 normal was added and the mixture was heated in a reflux apparatus for fully one hour in the boiling waterbath. The liquid still possessed a faint alkaline reaction but became neutral on our adding a trace of dilute acetic acid. On pouring it into water a very beautiful white mass was precipitated which was drained and then air-dried. Without being recrystallised it exhibited a melting point of  $52-53^\circ$ , showing it to be pure *p*-nitranisol.

On the other hand in this dilution benzene metanitrofluoride is but very little affected by treatment with sodium methoxide for one hour in the boiling waterbath:

1.0842 grams *m*- $\text{NO}_2$   $\text{C}_6\text{H}_4$   $\text{Fl} = 7.7$  millimols. were mixed with 10 c.c. of  $n/_{1.295}$   $\text{NaOCH}_3$  this being the equivalent quantity. After being diluted with water, the liquid was titrated back with 7.50 cc. of *n* acid, theory requiring 7.7 cc. Only 0.2 millimols of the compound had therefore, been decomposed, or 2.6% of the total amount.

This renders it possible to quantitatively determine the amount of benzene *p*- and *m*-nitrofluoride in a mixture of the two compounds as shown by the following experiments:

*a.* 1.1040 grams = 7.83 millimols. of a mixture of 89% of the para and 11% of the meta compound were mixed with 10.1 cc. of  $n/_{1.295}$  sodium methoxide and heated in a reflux apparatus for one hour in the boiling waterbath. After being poured into water the liquid was titrated back with 0.8 cc.

of *n* acid corresponding with 0.82 millimols of *meta* if we apply the correction of 2.6% for the *meta* compound attacked. 0.82 millimols = 10.5% of the *meta* compound.

b. 1.1250 grams = 7.98 millimols. of the said mixture were treated in an analogous manner with the equivalent quantity (16.9 cc.) of  $n_{2.12}$  sodium methoxide. The liquid was then titrated back with 0.85 cc. of *n* acid, corresponding, after applying the correction, with 0.87 millimols. of the *meta* compound, or 10.9%. Taking the mean of these two experiments we find 10.7% of the *meta*-compound.

Dr. BEEKMAN had observed that benzene dinitrofluoride (F1:NO<sub>2</sub>:NO<sub>2</sub> = 1 : 2 : 4) is converted at 15° in a few minutes into the corresponding anisol by the action of sodium methoxide. This circumstance might be taken advantage of for the quantitative determination of this dinitro compound in the presence of benzene *p*-nitrofluoride if the latter should suffer no change. This was, indeed, the case:

1.0035 grams of the *para* compound were treated at 15° for 5 minutes with 9.53 cc. of  $n_{1.91}$  = 5 cc. *n* sodium methoxide. After being poured into water the liquid was titrated back with 5 cc. of *n* acid.

A mixture of the two gave the following result:

1.1680 grams of a mixture containing 10.9% of the dinitro compound were digested at 15° for 5 minutes with 17.6 c.c. of  $n_{2.12}$  NaOCH<sub>3</sub>. The liquid was then titrated back with 7.6 cc. of *n* acid; there was, therefore, present a quantity of dinitro compound of  $\frac{17.6}{2.12} - 7.6 = 0.7$  millimols, or 0.1302 gram corresponding with 11.1% of the dinitro compound.

The above observations rendered it possible to quantitatively determine any benzene di- or metanitrofluoride eventually present in a nitration product of benzene fluoride. In order to determine the benzene orthonitrofluoride contained therein, I converted this into the dinitrocompound by renewed treatment of the nitration product with concentrated nitric acid. Dr. BEEKMAN had found that a further nitration took place (as shown by the increased sp. gr.) when the said product was treated for half an hour at 0° with five times its weight of nitric acid of 1.52 sp. gr., but that even after this treatment, traces of benzene orthonitrofluoride may still be detected by boiling the compound with aqueous sodium hydroxide which yields *o*-nitrophenol. On the other hand Dr. BEEKMAN showed that pure benzene *p*- and *m*-nitrofluoride are quite unaffected by this renewed treatment. In order to get a further and complete nitration of the ortho compound, I prolonged the time of the renewed treatment with nitric acid to one hour after first ascertaining whether benzene

*p*-nitrofluoride is unaffected thereby. This did not seem to be quite the case, so a small correction has to be applied:

*a.* 2.95 grams of pure *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Fl were treated at 0° with five times the weight of fuming nitric acid of 1.52 sp. gr. The compound rapidly dissolved without elevation of temperature. After one hour the liquid was poured into ice water and the fluorine derivative was instantly precipitated in a solid condition. When the liquid had become clear it was carefully filtered and the mass was repeatedly triturated in ice water until the acid reaction had completely disappeared. It was then treated with 9.65 cc. of *n*/<sub>1.93</sub> NaOCH<sub>3</sub> for 5 minutes at 15°. The liquid was then titrated back with 4.77 cc. of *n* acid. This gives  $\frac{9.65}{1.93} - 4.77 = 0.23$  cc. of *n* alkali consumed, corresponding with 0.428 gram of dinitro compound, or 1.4%.

*b.* 1.732 grams of the para compound were treated in the same manner. But after the acid had been removed by washing, the residue was melted to a clear liquid by applying a gentle heat. It was then cooled in ice water and again triturated and washed in ice water until the last traces of acid had disappeared: it was then treated as in *a.* 10.48 cc. of *n*/<sub>1.93</sub> NaOCH<sub>3</sub> were used and the liquid was titrated back with 5.3 cc. *n* acid; 0.1 cc. of *n* alkali had therefore been absorbed corresponding with 0.186 gram of dinitro compound or 1.0%. The mean of the two determinations is therefore 1.2%.

Being in possession of these data, I have now subjected the nitration product of benzene fluoride to the same test. Dr. BEEKMAN had previously found that the nitration at 0° with a mixture of 25 cc. of nitric acid of 1.48 sp.gr., 5 cc. acid of 1.51 sp. gr. and 10 grams of benzene fluoride yields a compound consisting solely of mononitro compound (to judge from its percentage of nitrogen; found 9.95 calculated 9.93). I, therefore, nitrated in the same manner and purified the product, which in ice water is semi-solid, by first washing it in ice water, being careful not to lose any oily globules, and then with water at 20°, which caused the whole mass to melt to a homogeneous liquid. After all acid reaction had disappeared the bulk of the water was removed by means of a separatory funnel, the clear pale yellow oil was freed from a few drops of adhering water by means of a strip of filterpaper and then finally heated in a testtube at 90°—100° until it no longer became hazy on cooling. We may assume that all the moisture has then been removed, likewise small quantities of any unchanged benzene fluoride. The product so obtained solidified after inoculation at 18°.7; a second preparation at 18°.6.

It does not contain benzene dinitrofluoride:

1.4115 grams were treated for 5 minutes with 9.45 cc. of *n*/<sub>1.93</sub> sodium methoxide. The liquid was titrated back with 4.9 cc. *n* acid, or 9.46 *n*/<sub>1.93</sub> acid.

But on the other hand it contains benzene metanitrofluoride:

*a.* 5.208 gram of the nitration product = 36.9 millimols. were heated with the equivalent quantity, namely 78.5 c.c., of  $n_{1.212}$  sodium methoxide for one hour in the boiling waterbath. After being poured into water, the liquid was titrated back with 1.5 c.c. *n* acid; this after correction corresponds with 0.2170 gram of meta compound or 4.2 %.

*b.* 5.817 gram of the nitration product = 41.3 millimols were treated in the same manner with the equivalent quantity, namely 79.7 cc. of  $n_{1.93}$  sodium methoxide. The liquid was titrated back with 1.55 c.c. *n* acid; which after correction for the attacked meta compound (2.6 %) corresponds with 0.2243 gram, or 3.9 % meta compound. The mean of the two determinations is, therefore, 4.1 %.

In this determination of the quantity of meta compound it has been assumed (and such is very probably the case) that the benzene orthonitrofluoride present in the nitration product also reacts quantitatively with sodium methoxide.

By renewed treatment of the nitration product with concentrated nitric acid in the manner described, its solidifying point does not perceptibly alter, for it was found to be at 18°.8. This had already been noticed by Dr. BEEKMAN. Still, the twice nitrated product now contains benzene dinitrofluoride:

*a.* 1.0015 gram of twice nitrated product was left in contact for 5 minutes at 15° with 8.45 cc. of  $n_{1.91}$  sodium methoxide. The liquid was titrated back with 3.9 cc. *n* acid. Therefore, alkali absorbed  $\frac{8.45}{1.91} - 3.9 = 0.5$  cc. *n* alkali = 0.093 gram dinitro compound, or 9.3 %.

*b.* 2.264 grams were treated in an analogous manner with 10.15 cc. of  $n_{1.91}$  sodium methoxide. The liquid was titrated back with 4.25 cc. *n* acid. Alkali consumed, therefore  $\frac{10.15}{1.91} - 4.25 = 1.06$  cc. corresponding with 0.197 gram, or 8.7 % dinitro compound. The mean of the two determinations is, therefore, 9.0 %.

Now we have seen that by treating pure benzene *p*-nitrofluoride with strong nitric acid for one hour 1.2% undergo further nitration. In the twice nitrated mixture there is present 9% of dinitro- and 4% of meta compound<sup>1)</sup>, therefore 87% of para; 1.2% of this represents 1% of the whole. This quantity of 1% must, therefore, be deducted from the amount of benzene dinitrofluoride found, in order to obtain the quantity which owes its existence solely to the

<sup>1)</sup> 9.0% dinitro = 6.4% mononitro. By subsequent nitration, 100 parts of the once-nitrated product increase to  $100 + (9.0 - 6.4)$  or 102.6 parts which contain 4.1 parts of meta, or 4%.

subsequent nitration of the benzene *o*-nitrofluoride. This, therefore, amounts to 8%, corresponding with 6.1% of ortho compound. According to the above the composition of the nitration product is therefore :

6.1%	benzene ortho nitro-fluoride	} Being formed by nitration of benzene fluoride at 0° with the concentration of the acid stated on p. 662.
4.1%	„ meta „	
89.8%	„ para „	

The composition of the twice nitrated product was found to be 9% of benzene dinitrofluoride, 4% of meta- and 87% of para compound. This was easily controlled by making an artificial mixture having this composition as all the three components were at disposal. Its properties must then be identical with that of the twice nitrated product. And indeed, the solidifying point of such a mixture was found to be 18°.7 and 18°.9 whilst that of the said product was at 18°.8. According to BEEKMAN'S data<sup>1)</sup>, the sp. gr. of the artificial mixture should amount to 1.2773, whereas 1.2791 was found for the twice nitrated product. This higher figure is, probably, to be attributed to the fact that the corrections to be applied are somewhat uncertain so that the results could only be accurate to within about 1%. If this should cause a little excess of dinitro and a little deficiency of meta compound, the sp. gr. will be at once seriously affected, whilst the solidifying point does not perceptibly alter. In fact, an excess of 0.8% of dinitro compound is sufficient to explain the difference in the sp. gr.

I have also endeavoured to nitrate benzene fluoride at -30°, using the same acid mixture employed in the nitration at 0°. On adding the fluoride drop by drop to the acid cooled to that temperature it dissolves with a dark brown colour causing but little rise in temperature, just as had been observed in the nitration of benzene bromide. After all the benzene fluoride had been added, the colour gradually began to fade and when the nitration vessel was removed from the refrigerating mixture and its contents reached a temperature of about -20°, the liquid soon became pale yellow and the temperature rose to about + 10°. It, therefore, appears that the velocity of nitration at -30° is already considerably retarded, as the introduction of each drop of benzene fluoride at 0° is accompanied by a very perceptible caloric effect. The solidifying point of the product which was collected in the way described, was situated at 19°.1, from which it may be concluded that it differs but little from the product obtained by nitration 0°. This can only contain about 1% less of by-products.

<sup>1)</sup> Sp. gr. meta 1.2532; para 1.2583; dinitro 1.4718, all at 84°.48.

Let us now see what the quantitative determinations of the nitration products of the halogen benzenes have taught us:

	$C_6H_5Fl.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5J.$	
ortho . . . .	6.4	29.8	37.6	34.2	} nitration temp. 0°.
meta. . . . .	4.4	0.3 (?)	0.3 (?)	—	
para. . . . .	89.8	69.9	62.4	65.8	
ortho . . . .	—	26.6	34.4	35.3	} nitration temp. -30°.
meta. . . . .	—	0.3 (?)	0.3 (?)	—	
para. . . . .	—	73.1	65.3	64.7	

From this nitration of benzene fluoride it is also shown in the plainest manner that the influence of the fluorine atom on the position of the nitro group is quite different from that of other halogens which in this respect behave very similarly.

*Groningen*, Dec. 1903.

*Lab. Univers.*

**Chemistry.** — “*Description of an apparatus for regulating the pressure when distilling under reduced pressure.*” By JAN RUTTEN. (Communicated by Prof. S. HOOGWERFF).

(Communicated in the meeting of February 27, 1904).

When distilling under reduced pressure it is always of importance to keep this constant during the distillation: moreover, the pressure during the operation must frequently be a definite one. This is, for instance, the case in the testing of mineral oils, where it is generally required that a definite quantity shall distill over at a definite pressure, which is in general considerably less than that of the atmosphere, and at a definite temperature.

As it is not possible to keep the pressure sufficiently constant by the admission of air, the quantity of which is regulated by a screw-

clamp, many apparatus have been recommended by various investigators in order to effect this purpose automatically<sup>1)</sup>.

As, however, these apparatus are either somewhat complicated or else do not always effect a satisfactory regulation of the pressure, and as I had very often to carry out distillations under reduced pressure, I have tried to construct an apparatus which would suit my purpose. I have used this apparatus for a year and a half and it quite satisfies my requirements.

The apparatus may be used for any pressure situated between that of a column of mercury of a few m.m. and one of about 600 m.m. in height; the required pressure is kept fairly accurately constant.

For the sake of clearness, the lower half of the annexed drawing represents a section of the apparatus and the upper half gives a view of the latter.

*A* is a glass tube with an internal diameter of about 19 mm. and to which is sealed a tube *B* 2 mm. wide; *H* is a trap-bulb; *C* a manometer tube which stands in the same mercury vessel as the barometer *D*. *A* is attached to the wooden piece *C* which may be moved in a vertical direction between the pieces *E'*. The tube *A* may be moved upwards and downwards by means of a wheel. *A* is placed in a vessel partly filled with mercury; the lower opening of *A* is closed with an indiarubber stopper having a vertical hole of about 5 mm. diameter. To the extremity of the thin tube *B* a piece *E* is connected; *E* is made of wood, cork or rubber and has a vertical perforation by means of which it may be pulled over the tube *B*. It has in addition a side  $\wedge$  (triangular) crevice running as far as the vertical perforation. The proper action of the instrument depends on the piece *E*.

Between the tube *C* and the barometer *D* is situated a calibrated scale movable in a vertical direction by means of *L*, which renders an accurate reading of the pressure possible. From the drawing it is further shown, that *A* and *C* are connected by means of glass  $\Gamma$  pieces and of thick indiarubber tubes, not only mutually, but also with the airpump and the space to be evacuated. (So as not to

1) KAMERLINGH ONNES, These Proc. June 1903

STAEDEL & HAHN, Liebigs Ann. 195 p. 218.

GODEFROY, Ann. Chem. Phys. [6] 1884 — 1 — p. 138.

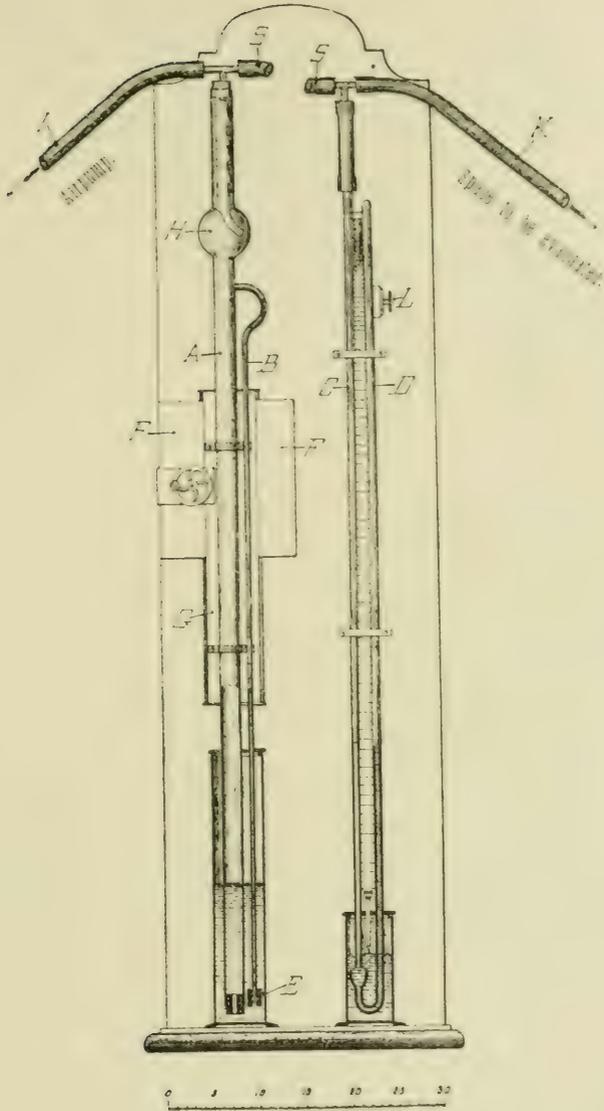
AUGER, Bull. Soc. Chem. [3] 1898 — 19 — p. 731.

HAUSSER, Bull. Soc. Chem. [3] 1899 — 21 — p. 253.

BERTRAND, Bull. Soc. Chem. [3] 1903 — 29/30 — p. 776.

Chem. Centr. 1903 — 2 — p. 611.

A. SMITS, These Proc. 27-11-1897.



spoil the drawing, the tube has been cut near *S*; one must imagine between the two *S*'s a piece of tubing, about 50 c.m. long). Neither the lower nor the upper side of *A* has been narrowed, so as to facilitate the cleaning of the tube.

After the mercury vessels have been properly filled and the apparatus connected, the air is rarefied by means of a powerfully acting removable water-pump. In consequence the mercury rises in *A*, *B* and *C*.

When the requisite pressure is attained, *A* is raised by means of

the wheel until the point of the triangular opening of the piece *E* just reaches above the mercury. This will be observed at once as a current of air and mercury then passes from *B* towards *H*. If for some reason the division of air and mercury does not take place at once, a tapping of *B* is sufficient to effect this. The mercury which is carried over, is thrown forcibly against the side of *H*, but this being constructed as a trap, no mercury can be carried over with the escaping air through *I* or *K*.

If the desired pressure is not yet attained, *A* is turned lower or higher, should the pressure be still too great or too small. But once the required pressure attained, it will remain constant as air is being continuously admitted through *B*.

Suppose, for instance, that, owing to incipient decomposition, badly condensable gases are formed during the distillation, the mercury falls in *A*; the additional mercury now arriving in the mercury vessel renders the part of the  $\wedge$  shaped opening, which projected above the mercury, smaller and in consequence less air can proceed from *B* to *H*; unless the power of the waterpump is exceeded the original pressure will be maintained. If such is not the case the original pressure must be again restored by moving *A*.

Instead of the barometer and the manometer tube a shortened pressure gauge with movable scale (like the gauge of an airpump) may be employed <sup>1)</sup>.

**Physics.** — “*Methods and apparatus used in the cryogenic laboratory VI. The methylchloride circulation.*” By Prof. H. KAMERLINGH ONNES. (Comm. N<sup>o</sup>. 87 from the physical Laboratory at Leiden).

(Communicated in the meeting of June 27, 1903).

§ 1. *The methylchloride boiling vessel.* In Comm. N<sup>o</sup> 14 Dec. '94 in the description of the cascade of circulations which produces the permanent bath of liquid oxygen for different measurements, I have mentioned that the methylchloride refrigerator used there left much to be desired. At the time when I arranged the cryogenic laboratory at Leiden, the use of liquefied ethylene in a circulation to obtain an efficient circulation of liquid oxygen was an untouched scientific problem. As a result my attention was principally concentrated — besides on the question of obtaining a permanent bath of liquid

<sup>1)</sup> The apparatus may be obtained from the Ned. Instrumenten Fabriek, Utrecht, Holland.

oxygen — on the ethylene circulation, so that this might be made a type of a low temperature circulation with a small quantity of working gas. The removal of the principal deficiencies of PICTET's first cycle in place of which my methylchloride cycle is used, was thus, as far as possible, deferred until an ethylene condensation was required quicker than the one then necessary.

One important improvement in the cascade method could not be dispensed with even then in the methylchloride circulation, if I wished to work with success. It was the introduction of a regenerator with the methylchloride refrigerator. Regenerators had been already, as I found later, used or patented by SIEMENS and SOLVAY for freezing-machines. Still it appears that they were first used by me for the systematic production of liquefied gases, and that the combination of regenerators with the cascade method, in addition to my other auxiliary apparatus, first made this method practical.

The regenerator, where the vapour rising from the methylchloride cools the ethylene which proceeds to the condenser immersed in methylchloride, has been very curtly mentioned in Comm. N° 14 (Dec. '94). It is shown on Pl. IV of Comm. N° 51, Sept. '99 and on Pl. II of the present communication, where further under  $\mathfrak{D}$  the same letters will be found as employed in Comm. N° 51. In the following the details are always indicated by suffixes to the Gothic letters which are used as distinctive for the various kinds of apparatus.  $\mathfrak{D}_F$  is the well known PICTET refrigerator (first designed for sulphur dioxide),  $\mathfrak{D}_E$  the regenerator. The liquid methylchloride flows into the condenser through  $\mathfrak{D}_I$  (*I* cf. Comm. N° 51), and is pumped away through  $\mathfrak{D}_K$ . The spiral within the regenerator contains  $N_2O$  in the case represented in the plate (represented by doubly marked lines).

This refrigerator and regenerator is now almost exclusively used for the production of liquid  $N_2O$  (c.f. Comm. N° 51 Sept. '99). A refrigerator and regenerator with a much larger working surface and a better construction is combined with the condenser and its pump for use with liquid ethylene. These were constructed with great care by the mechanist of the cryogenic laboratory Mr. G. J. FLIM. Their description has now become necessary, since the increased rapidity with which this quantity of ethylene can be circulated by their means has rendered many recent measurements possible.

The ethylene boiling vessel <sup>1)</sup> of § 5 Comm. N° 14 Dec. '94 served as a model for the new arrangement. In that model the regenerator and refrigerator have been combined to a single piece of apparatus.

<sup>1)</sup> Represented in the account by MATTHIAS, Rev. Gen. des Sciences 30 April 1893, p. 385.

In the same way the regenerator and refrigerator for methylchloride are combined (see  $\text{\textcircled{E}}$  Pl. II for the elevation and Pl. I for the section) in one apparatus which we will call the methylchloride boiling vessel. The experience with the ethylene boiling vessel has been put to use, so that in its turn also the methylchloride apparatus will serve as a model for an improved ethylene boiling vessel. The increase of the ratio between the surfaces of regenerator and refrigerator allows the methylchloride to leave the apparatus at nearly ordinary temperature, even when the BURCKHARDT pump as described Comm. N<sup>o</sup> 83 Apr. '03 sucks with its full force; which could not be obtained before with the ethylene boiling vessel. The condensing surface measured in the tube is about 0.9 M<sup>2</sup>., and the regenerator surface, similarly measured, nearly the same.

The walls of the boiling vessel are soldered to form one whole; those of the refrigerator  $Ca_{10}$  and  $Da$  (see Pl. I) are of copper 1 mm. thick, that of the refrigerator  $Fa$  of thin brass 0.5 mm. thick. The neck  $E$  of the refrigerator is soldered to the regenerator and this again to the mouthpiece  $Ga$ . Owing to the length of the regenerator and the thinness of the walls it is possible to make the latter of brass. Even with this material the heat conduction is of no importance. Since the vessel must be evacuated it must show a considerable resistance to external pressure. The resistance of the walls themselves is in the first place increased by the addition of small ridges which are shown as  $Ca_{11}$  in the main drawing with the detail of the wall to the right and the section to the left. In the conical space  $D$  six triangular copper plates  $D_{b_{10}}$  (cf. principal figure and the section at bottom right of Pl. I) give the necessary stiffness. These have flanges  $D_{b_{11}}$ ,  $D_{b_{12}}$ , which rest on one side on the bottom, on the other side they carry the conical wall of the vessel through three rings  $D_{c_1}$ ,  $D_{c_2}$  and  $D_{c_3}$ . Resistance to outward pressure, which becomes necessary when leaks have to be sought, is provided by pressing the bottom of the refrigerator against the plates  $D_{b_{10}}$  by means of four wooden balks  $Ca_d$ , which also protect  $Ca_{a_4}$ , pressing on crossed laths  $C_b$  which are screwed up to rest on the round upper surface by means of steel rods  $C_{c_3}$  and a ring  $C_{c_0}$ .

In contrast with the scheme of the ethylene boiling vessel, it was not considered necessary that the height of the liquid should remain very little above the windings of the condensation spiral. To condense oxygen in the ethylene boiling vessel it was of all importance that the temperature of the condensation spiral should fall as far as possible and thus that the ethylene should boil under a very low pressure. Now in that case there would be no advantage in the vacuum pump

removing the vapour under very low pressure, which implies a rather considerable loss of work by friction, if boiling nevertheless occurred at a higher pressure. And this must occur when to the suction pressure was to be added a noticeable hydrostatic pressure due to the turns of the condensationspiral, where the vapour forms, being much beneath the surface of the evaporating liquid. In the case of the methylechloride circulation it seemed to me that the obtaining of the lowest possible temperature was not of utmost importance and that there was no objection to simplify the construction by allowing liquid to be introduced to a height of 20 cm. in the refrigerator, though not all profit is taken in this way of the low pressure (at most 20 mm. of mercury) under which the BURCKHARDT—WEISS vacuum pump, which is introduced into the methylechloride circulation, sucks at full speed (usually about 8 mm. is employed).

The spiral where the ethylene is liquefied (length 53 m., inner diameter 6.4 mm., thickness of wall 0.8 mm.) lies in two windings in the hollow cylindrical mantel  $C'$  in which the conical refrigerating vessel  $D$  terminates below. There is just room between the two windings of the spiral (see section bottom left below and the elevation of the section through  $D$  bottom right on the plate) for the ascending tube  $Ad$  by which the lower end of the inner spiral  $Ac Ad$  is joined to the upper end of the outer. These two cylindrically wound spirals are joined to a flat spiral  $Ac$  which lies on the bottom of the boiling vessel. When the latter is well filled this spiral lies just under the surface of the liquefied gas introduced through the cock  $N$ . The spirals are coupled so that the liquid is driven out by the pressure of the gas. If the boiling vessel is always kept so full that the flat spiral is immersed, it is advantageous to let out the condensed gas from the last spiral. Should it be desirable to work with a smaller quantity, it is better to first run the gas to be condensed through the flat spiral; this case is shown in the drawing. If the flat spiral is immersed the temperature (usually  $-87^{\circ}\text{C.}$ ) of the liquid can be read on the thermometer  $O$ , the stem of which is bent for convenience and is immersed in the tube  $D_{d_1}$  filled with alcohol and protected from interchange of temperature with the air by means of an ebonite tube  $D_{d_2}$  joined to it with fish glue. The capacity for liquefied gas when the cylinder- and flat spirals are covered is 6 liters, the volume of the spiral 1 liter.

The conical space of the refrigerator is sufficient even for an excessive boiling up of the liquid, which is always large at low temperatures as can be seen from the movements of the float.

The regenerator spiral consists of two long tubes  $B_{b_1}$  and  $B_{b_2}$  39 m.

and  $B_c$  and  $B_d$  19 m. respectively, which are wound in the space between the outer wall  $F_a$  of the regenerator and the very thin walled inner cylinder  $H$ , divided into three parts by two wooden rings. The inner diameter of the tubes is 7.5 mm., the walls are 1 mm. thick. The two spirals can be joined otherwise than in the manner shown in the figure, but further description is unnecessary. A safety cap  $A_a$  (c.f. the ethylene boiling vessel Comm. N<sup>o</sup>. 14 § 5) is also joined to the spiral, so that the bursting of the spirals within the boiling vessel is not possible. The figure shows clearly how, without a complicated construction, an intimate contact between the rising vapour with the regenerator spiral is produced and also a constant intermixture of the vapour partially warmed by contact with the metal and of the still unheated portions, convection currents which extend to some distance being avoided.

The interchange of heat between the vapour, which rises in the regenerator, and the gas which is put into the spiral is furthered without appreciable loss of pressure by friction, by laying a perforated copper plate  $B_{b_2}$ , through which the spiral find its way, horizontally above each lattice spiral  $B_{b_1}$  (see detail right section and plan). This plate is soldered to the spiral where it turns downwards. In the detail figure to the right, section and view above a plate, the soldering place can be seen to the right of  $B_{b_3}$  at the vertical section of the spiral. In this figure the perforations are only drawn over a small portion of the plate for simplicity. The perforated plate is insulated by wooden blocks  $B_{b_1}$  from the adjacent lattice, against which these blocks press. Further cotton and parchment paper are wrapped round the column of plates and thus the spiral with the plates is made to a whole that just fits into the regenerator space. In this way the gas, finding the way through the inner cylinder shut, can only escape through the perforated plates. The inner cylinder is insulated by paper from the perforated plates, and is usually closed above by  $H_l$ . Should it have to sustain pressure owing to perhaps a sudden violent development of vapour, or owing to the closure of a sieve plate by the freezing of moisture the vapour can immediately escape through the safety valve  $H_{b_1}$ , the construction of which is shown sufficiently in the drawing.

The whole boiling vessel hangs on the solid neck  $G_a$ , along which the vapour escapes, in the same manner as the ethylene boiling vessel  $G_a$  rests with a collar  $G_c$  on a bracket (see Pl. II). The main outlet tube  $G_a$  gives off a branch through a large but light cock  $I$  — the construction of which is sufficiently shown on the drawing

— to the wide feeding tube of the BURCHHARDT—WEISS vacuum pump ( $\mathfrak{A}$  Pl. II), arranged as described in Comm. N<sup>o</sup>. 83.

A second narrower branch with ordinary cock  $L$  runs to one of the combined pumps of the Société Gènevoise, mentioned in Comm. N<sup>o</sup>. 14.

On commencing to work with the methylechloride circulation  $\mathfrak{B}$  is used alone, afterwards  $\mathfrak{A}$  and  $\mathfrak{B}$  in series. Naturally when no more liquid ethylene is required than was formerly used (Comm. No. 14 Dec. '94) the pump  $\mathfrak{B}$  can be used alone and  $\mathfrak{B}_T$  (Pl. II) remains closed.

A third branch  $Gf'$  goes to the safety cap  $K$ , the construction of which is sufficiently shown in the diagram, and as soon as the pressure reaches above the atmospheric the vapour is conveyed into large rubber sacks  $\mathfrak{H}$  of 500 liters capacity each which are themselves connected with a safety tube  $\mathfrak{H}_t$ .

If a sudden violent development of vapour occurs or the outlet becomes closed unexpectedly, the vapour can escape through the safetycap  $M$  Pl. I. The arrangement of this can be seen from the detailed drawing near  $M$ . The caoutchouc sheet  $M_{l_1}$  covered on its lower surface by a tin plate nearly up to the sides, and fixed to the rim  $M_a$  (on which a rim is turned to prevent lateral motion), rests on the perforated plate  $M_e$  and is thus protected from the effect of exhausting the vessel. It is also not blown out by pressure as it is pressed by the cap  $M_d$ . As soon as the pressure rises above that at which the spring is set (0,15 Ats above the atmospheric) the catch on which the spring presses flies open, the cap is driven upwards and the caoutchouc bursts.

The soldered connection between the main outlet tube and the regenerator is not exposed to strain since above and below the latter, stout wooden rings  $F_d F_e$  are laid and strengthened with iron bands  $F_{g_1} F_{g_2}$ . The upper is fastened to the cover by three rings  $R_1$ , the lower is drawn against the upper by steel wires  $F'_{j_{10}}$  at constant tension temperature, changes being allowed for by springs  $F'_{j_{11}}$ . The tension is adjusted to the mean of the weight of the whole apparatus and that of the regenerator. The lower ring  $F_{g_1}$  just mentioned is fixed sideways by bands  $S_a$  and  $S_d$  (see chief figure and detailed figure to left), it carries further another iron band  $S_c$  onto which various cocks are fixed (see also Pl. II,  $\mathfrak{E}$ ).

The cock  $N$  to admit methylechloride is also fixed on an extension  $S_c$  of this ring. The most advantageous cock would be one constructed in the manner of that on the ethylene boiling vessel (see MATHIUS description l. c. p. 385). It is however sufficient that it should have the construction of that at  $\mathfrak{D}$  (Pl. II. of this and Pl. IV of Comm.

Nr. 51, and shown in detail in the above mentioned description l.c. p. 383 Nr. 7).

The long pin (see Pl. I).  $N_a$  runs first through the inlet tube  $N_{b_{10}}$ , continued by  $N_{10}$  for the methylchloride and is pressed against the opening in the bottom  $N_{b_{11}}$  of the tube  $N_{b_{10}}$  by means of a screw in  $N_{b_{01}}$  above the side inlet tube  $N_e$  for methylchloride. The tube with cock  $N_b$  rests loosely in the special tube  $D_{e_1}$ . The joint is closed by caoutchouc  $D_{e_2}$  on the enlargement  $N_{b_{02}}$  and allowance is made in this manner for the relative shifting of the tubes owing to change of temperature.

This arrangement is used when methylchloride at the ordinary temperature is admitted to the apparatus. The cock  $N$  insulated from the tube  $D_e$  is kept at the ordinary temperature by the thick iron ring  $S_c$  and the caoutchouc at the upper end thus remains soft while otherwise having become brittle by cooling it would break owing to the unequal displacement of  $N$  and  $D_e$ . It is always necessary to introduce the methylchloride at the ordinary temperature when it is not quite pure and dry, otherwise the cock will be frozen fast. A cock of the model  $N$  is very appropriated for the admission of methylchloride at the ordinary temperature.

A good method for purifying the necessary quantity of methylchloride consists in drawing off the methylchloride in the boiling vessel by means of the cock  $N$  and causing it to evaporate by condensing ethylene in the spiral. If the cock freezes, the pressure is made equal to that of the atmosphere by shutting  $L$  off, or if necessary bringing the apparatus in connection with the sacks  $\mathfrak{H}$  (Pl. II.) through  $L$ .  $N$  can then be taken out of  $D_c$ . Before using the flask after a process of purification it is first dried by the aid of the tube and cock  $T_a$ .

If the methylchloride is first cooled by contact with a cold gas, as is shown at  $\mathfrak{E}'$  on Pl. II next to the principal drawing, the inlet tube passes through an ordinary cock  $N_1$ .

The cock  $T_b$  serves to introduce the ethylene to be condensed, the cock  $T_c$ , which is placed on wood and packed in wool, to draw it off.

The cock  $T_a$  is inserted in the tube  $A_b$ , which runs to the bottom of the cylindrical space  $C$  and is used for cleaning and drying.

The position of the liquid methylchloride can be seen from the float  $P_1$ , which moves up and down in the central tube  $C_{a_3}$ , itself in connection with the space round the spiral through the tube  $C_{a_4}$ . By means of an aluminium wire, a silk cord and a platinum wire,  $P_2$  is joined to a silk cord  $P_3$ , which passes over the pulley  $Q_b$  into the glass tube  $Q_a$ , where it is attached to a weight  $P_4$  which runs along a scale fixed to the tube  $Q_a$ .

The flask is packed in the same way as the ethylene boiling vessel (Comm. N<sup>o</sup> 14) first with nickel paper and then with several layers of wool, the number of layers increasing at the colder parts, as can be seen from the drawing Pl. I. They are contained between varnished and nickelled paper as is seen in  $C_h$ ,  $C_i$ ,  $C_k$ ,  $C$ ,  $F_h$ ,  $F_i$ ,  $F_k$ , while horizontal strips of felt, dotted in the drawing, prevent convection currents. These various layers form airtight compartments, which are connected together by means of small tubes  $C_m$   $C_n$ , while the whole airtight space is connected with the atmosphere through a drying tube  $Fl$ . The outer surface is painted white.

§ 2. *The methylchloride cycle.* A short description of this is desirable. The liquid methylchloride is preserved in the tubulated condenser  $\mathfrak{G}$ , which is cooled by running water. Its pressure is measured by the manometer and its level can be seen in the level glass  $\mathfrak{G}_p$ , with blow-off cocks as used with water boilers (to make a reading the connecting tube for liquid methylchloride  $\mathfrak{G}_1$  must be cooled with ice as shown diagrammatically on Pl. II (for further particulars the quoted description of MATHIAS p. 383 N<sup>o</sup> 2)). A large cock  $\mathfrak{G}_1$  protected by a filter (shown l.c. as N<sup>o</sup> 9) makes it possible to shut the condenser off immediately by a small movement, even when a strong stream of methylchloride is sent through the condenser. This cock is followed by a regulating cock  $\mathfrak{G}_2$  to which the tubes for liquid methylchloride are connected. The latter run to:

1<sup>st</sup>. the refrigerator  $\mathfrak{D}$ , which is used to obtain liquid nitrous oxide, either in the manner given in Comm. N<sup>o</sup> 51 Sept. '99, or by drawing it off into a vacuum vessel  $\mathfrak{U}$  from which the nitrous oxide can be siphoned over into other vacuum vessels and thus be brought to apparatus arranged in other rooms.

As far as the nitrous oxide circulation according to Comm. N<sup>o</sup> 51 is concerned the mercury and auxiliary compressors (Comm. N<sup>o</sup> 54) can be used as  $\mathfrak{X}$  in place of the BROTHERHOOD of Comm. N<sup>o</sup>. 51.

The various pieces of apparatus, for which the nitrous oxide in  $\mathfrak{U}$  is used, are generally connected to the tube  $App$  and the sack  $\mathfrak{B}$  from which the gas can be repumped into  $\mathfrak{B}$ . Plate II shows the use of a small 2 K.G. cylinder  $\mathfrak{B}$  of the kind usually used in this laboratory for this purpose.

2<sup>nd</sup>. other apparatus formerly described e.g. one of the cryostats (Comms. N<sup>o</sup> 51 and 83),

3<sup>rd</sup>. the boiling vessel for the preparation of liquid ethylene  $\mathfrak{C}$  Pl. II as described in § 1, either directly or through the regenerator  $\mathfrak{C}'$  where the methylchloride is cooled by cold vapour coming from another vessel and passing from  $In$  to  $Ex$ ,

4<sup>th</sup>. an apparatus  $\mathfrak{M}$  which will be described in detail in the following section and intended to deliver a stream of calciumchloride solution at a low but very constant temperature.

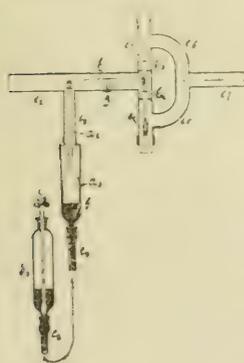
We may consider the methylchloride vapour which streams out of these refrigerators and regenerators. In the case 3 above (sometimes also in case 2 for which the connection  $\mathfrak{B}_i$  serves) it would be sucked by a BURCKHARDT—WEISS vacuum pump  $\mathfrak{A}$ , installed in the manner given in Comm. No. 83. From here it would travel to one of the conjugated pumps of the Société Génèvoise  $\mathfrak{B}$ , mentioned in Comm. No. 14, which receive the vapour from the BURCKHARDT or from all other apparatus ( $\mathfrak{D}$  Pl. II and further indicated under 2). This pump  $\mathfrak{B}$  may for another example take the vapour directly from the boiling vessel  $\mathfrak{C}$  (see Pl. II and *L* Pl. I) as well as between the high and low pressure cylinder from the branch tube  $\mathfrak{F}_1$  which too allows gas to be pumped from one of the four above mentioned sacks  $\mathfrak{H}$ , in which the methylchloride can be preserved for a short time and of which only one is represented on Pl. II, while other sacks can be connected to apparatus from which methylchloride escapes under constant pressure. The pump is provided with an indicator on the low pressure cylinder, a vacuummeter between the high and low pressure cylinders and a manometer on the high pressure cylinder, besides several cocks which are required for pumping, drying and filling with methylchloride. The vacuum meter  $\mathfrak{E}_{mm}$  indicates the pressure of the gas which enters the high pressure cylinder. From the cylinder volume and the number of strokes one can derive the volume of gas and reduce it to that under normal conditions moved in the cycle, so that the velocity with which the liquid in the refrigerator evaporates can be followed.

In addition a safety valve  $\mathfrak{B}w$  is added to the high pressure cylinder principally to protect the condenser  $\mathfrak{B}$ .

The methylchloride which can escape from this safety valve is passed into the above mentioned sacks  $\mathfrak{H}$ . Usually, all the methylchloride passes into the condenser, where it is cooled by running water from the main. In between, an oil trap  $\mathfrak{F}$  is placed which is slightly warmed by steam (see  $\mathfrak{C}_{vap}$ ), so that the transported oil shall give up the dissolved methylchloride. The oil thus separated by the change of direction is run into a flask  $\mathfrak{R}$ . The last portion of the methylchloride, freed here, is carried to the sack  $\mathfrak{H}$ . At the top of the oil trap, the gas is freed from the last traces of oil by layers of felt and wadding contained between sheets of metal gauze. (C.f. the oil trap of the ethylene circulation shown by MATTHIAS l.c. p. 383 fig. 1).

§ 3. *Circulation of calcium chloride solution at constant temperature below zero C.* The thermostat is similar to that described in Comm. No. 70 III May '01, but with the difference that at  $P_1$  a side tube with cock and mercury reservoir is introduced, so that the regulator can be set for high temperatures (very well to  $60^\circ$  C.) and also for a low one by the choice of a suitable fluid. The spiral is filled with benzene and, instead of water from the main (as in No. 70), a cooled stream of calcium chloride solution is run into the heating vessel. The solution is contained in a vessel  $\mathfrak{R}$  with filter and float  $\mathfrak{R}a$  and is driven through the refrigerator  $\mathfrak{E}_a$  and regenerator  $\mathfrak{E}_c$  in which the methylchloride evaporates and thus cools the circulating calcium chloride solution. This is caused to move by a force pump  $\mathfrak{E}$  with valves  $\mathfrak{E}_f$  connected to one of the conjugated compressors  $\mathfrak{B}$  while a bent tube prevents the cooled solution from falling.

In the refrigerator the liquid methylchloride runs through the tube  $\mathfrak{E}_{d_1}$  and regulating cock  $\mathfrak{E}_{d_2}$  to the inner space, while the calcium chloride solution runs spirally in the outer. The liquid methylchloride running into the refrigerator is cooled by the vapour evolved, which escapes by a wider tube  $\mathfrak{E}_b$  to the regenerator, from which projected liquid returns by a narrow tube  $\mathfrak{E}_h$ . Finally the danger which might arise when the cooled methylchloride, left between the cocks  $d$  and the shut off cock of the tubing  $\mathfrak{E}$ , returned to the ordinary temperature, is avoided by connecting a safety cap with a closed tube  $\mathfrak{E}_k$  added above. At 12 Atm. the thin plate breaks and sufficient space is produced without communication with the air. The walls are all calculated to stand the ordinary pressure of the methylchloride.



The pressure under which methylchloride evaporates must not fall below a certain value, as the calcium chloride might then freeze out. It is kept constant by the pressure regulator  $\mathfrak{E}$  Pl. II. When the pressure falls the mercury rises in  $b$ , see accompanying figure, and forces the float  $a_1$  upwards, so that the lever  $f$  rotates about  $g$  and thus closes the suction channel by the double valve  $h_1 h_2$ . A safety tube  $\mathfrak{E}'$  Pl. II and a tube to receive spilt mercury complete the apparatus. The properly cooled calcium

chloride solution runs from the refrigerator  $\mathfrak{E}_a$  to the thermostat  $\mathfrak{M}$ , where it is rewarmed to the required low temperature and conducted to the apparatus which must be held at constant temperature.

On Pl. II a piezometer surrounded by a vacuumglass is shown,

where the outer surfaces are connected by the copper box used for the vacuum jacket of Comm. N<sup>o</sup>. 85. This jacket remains free from dew deposit, so that the divisions on the tube can be clearly read. Above the liquid surface the vacuum tube is lengthened by an ordinary tube of about 50 cm, so that the solution is protected from the atmosphere by a layer of cold air.

The apparatus was e.g. placed once at about 25 meters distance from the refrigerator, in another room. It would be less suitable to convey the methylchloride itself over this long distance owing to the increased danger from fire.

The calcium chloride solution had a specific density of 1.28, the vacuum under which the combined pumps worked was set so as to produce a temperature of  $-45^{\circ}$  C. in the refrigerator and remained satisfactorily constant. The small pump moves about 2 liters of solution per minute.

In order to keep temperatures below  $-20^{\circ}$  C. constant at long distances by a methylchloride circulation, it will be necessary to have a refrigerator with a greater cooling surface.

**Physics.** — Communication N<sup>o</sup> 86 from the Physical Laboratory at Leiden. "*The representation of the continuity of the liquid and gaseous conditions on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of GIBBS*" (By Prof. H. KAMERLINGH ONNES and Dr. H. HAPPEL).

(Communicated in the meeting of June 27, 1903).

§ 1. The meaning of the following research will be best made clear by showing its relation to the former communications (66, 71, 74) from one of us (H. K. O.). Like these it arises from the certainty that it is increasingly necessary to represent the experimental values for an equation of state from a general point of view.

In the first place this research is connected with that of N<sup>o</sup>. 66<sup>1)</sup> on the reduced  $\eta$ ,  $\epsilon$ ,  $v$  ( $\eta$  = entropy,  $\epsilon$  = energy,  $v$  = volume) GIBBS' surface formed after VAN DER WAALS' original equation of state.

The drawings of N<sup>o</sup>. 66 show that a ridge appears on the side of small volumes on the GIBBS' surface given there, by shifting the constant isotherm (fig. 1) of simple form (i.e. Pl. I and II), derived from the above mentioned equation of state, along a vertical directrix.

<sup>1)</sup> KAMERLINGH ONNES, Die reducirten GIBBS'schen Flächen. Vol. jub. LORENTZ, Archiv. Néerl. Sér. II, T. V. p. 665—678. Leiden, Comm. n<sup>o</sup>. 66.

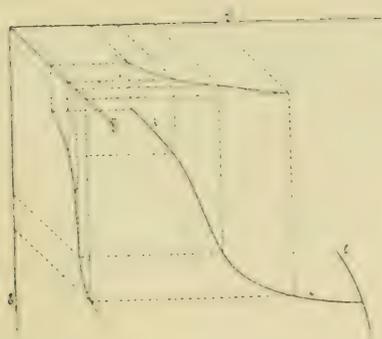


Fig. 1.

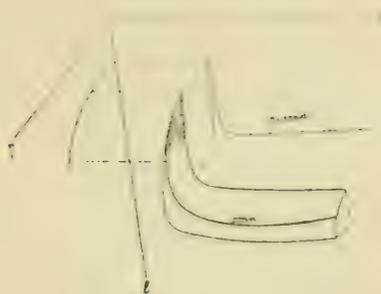


Fig. 2.

This ridge — the liquid ridge — carries the liquid branch of the connodal of the liquid vapour plait; the isotherms run over the ridge from the vapour to the liquid side and from higher to lower entropy (l. c. Pl. I, fig. 1.). In the vicinity of the critical temperature the ridge becomes broader and smoothes down into the double convex surface (l. c. Pl. I, fig. 3) which further forward is everywhere double convex. For lower reduced temperatures the ridge passes nearly into an  $\eta \varepsilon$  plane. The projection of the ridge on this plane is a curve along which the inclination ( $\text{tang}^{-1} = \text{absolute temperature } T$ ) decreases towards negative values of the entropy (see fig. 2). The projection of a cross section of the ridge shows the rapid change of the inclination in the  $v \varepsilon$  plane ( $\text{tang}^{-1} = \text{pressure } p$ ) for a small change of volume. The correspondence of the properties expansion, compressibility and specific heat, for liquid and solid shows immediately that the representation in the  $\eta, \varepsilon, v$  coordinatesystem of the experimentally determined conditions, belonging to one of the solid aggregations of a material, can be supposed to belong to a ridge corresponding to the liquid ridge. Also that other solid varieties require further ridges. So long as we exclusively keep to the experimentally determined values only narrow strips of these supposed ridges are given for a short distance to the side of the tops and thus form themselves isolated parts, not connected with the vapour and liquid regions, of the whole GIBBS' surface for the special substance.

The various ridges, if we for a moment admit their existence, will be more or less shifted, according to the density, towards zero volume ( $v$ ) and according to the fusion and transformation heats more or less to zero entropy ( $\eta$ ). The difference in specific heat of the modifications, will be given by a variation in curvature. Looking

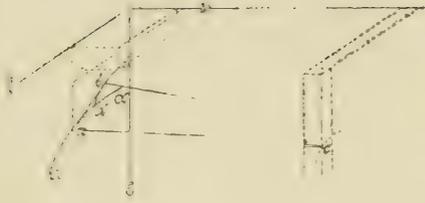


Fig. 3.

To find the coexisting phases from the region  $a' a''$  or from the region  $b'$  with the vapour phase from the region  $c$ , one must lay the common tangent plane on the curved surface in  $c$  and the given ridge. In the case that a rarefied gas phase occurs in  $c$ , the ridges would be represented approximately by curved lines. This is then also to be permitted in the search for the corners  $a$  and  $b$  of the fundamental triangle of the triple point. The general thermodynamical character of a solid state occurring together with the VAN DER WAALS state (liquid, gas and labile intermediate states) would be thus obtained by representing it on a GIBBS' surface by a ridge of a somewhat other position and form but generally analagous to the liquid ridge.

There is thus every reason to suppose that outside the region of observations and towards the large volumes the first continuations of the isotherms obey an analogous law as to form and change of form with temperature as the liquid isotherms, and thus by a slight extension really produce a ridge. This appears to be more probable when one notices that there is also a ridge on the GIBBS' surface which does not correspond to the original equation of VAN DER WAALS where  $a$  and  $b$  are taken as unchangeable but which belongs to the equation into which this changes when  $a$  and  $b$  are taken as functions of temperature and volume. Thus when shifting the variable or corrected isotherms (cf. N<sup>o</sup>. 66 § 3 end) in place of the original constant one a similar ridge as that which we have considered would also be always formed, though the successive isotherms are no longer equal and similar, but show a small continuous change with temperature. In this way one cannot escape the conclusion that metastable states occur at the side of the solid state between solid and gas.

The observed part of the isotherm on the vapour side for temperatures far below the furthest limit of the observed undercooling of liquid does not extend beyond the sublimation line. Still from analogy with what is known for vapour at higher temperatures, it must be assumed until the contrary is proved, that the GIBBS' surface extends inside the sublimation line to metastable and even to labile equili-

from the side of large  $v$ , we should see a succession of ridges, and where we for simplicity consider the case of a single solid state of aggregation, we should see the resulting ridge rising at lower temperatures above the liquid ridge (cf. fig. 3).

bria, not in principle different from those given by VAN DER WAALS' theory. And very clear and special evidence must be brought forward (which is not the case (cf. § 2)) to show that the two above mentioned parts of an isotherm must not be united.

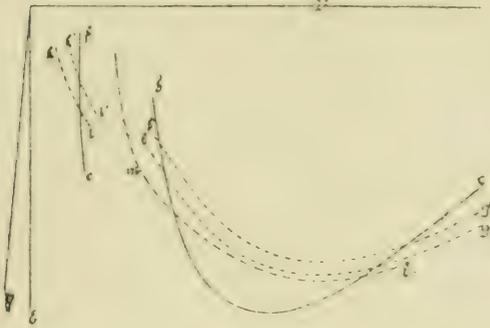


Fig. 4.

Now, (cf. fig. 4) for a substance which exists in the liquid and solid states, call  $cd$  and  $ef$  the portions of the connodal of the liquid and solid ridges,  $gh$  and  $ik$  portions of isotherms on the liquid and solid ridges. It is clear that  $i$  and  $h$  may be joined by a continuous line.

For the formation of two ridges it is clearly only necessary,

that two isotherms  $g'h'$ ,  $i'k'$ , should incline to the  $v$ -axis very strongly, but still not differ much from the two preceding isotherms  $gh$ ,  $ik$ , and also that  $h'i'$ ,  $hi$  should not differ much. With such small variations resulting from the above mentioned controlled changes of the isotherms with the temperature on the GIBBS' surface, we are very familiar since the  $a$  and  $b$  of VAN DER WAALS are taken as temperature functions. The difference between  $ik$  and the isotherm  $gh$  is analogous to the difference between the true empirical isotherm  $gh$  and the simplest form of isotherm given by VAN DER WAALS who has long shown that  $b$  must necessarily be a volume function. The portion  $hi$  alone appears to have received a somewhat greater change which we may ascribe to a further change of  $b$ <sup>1)</sup> with the volume.

With this explanation of the cause for the displacement of the isotherm on the GIBBS' surface we do not come into collision with the assumptions of VAN DER WAALS, who assumes that  $b$  undergoes a change in the fluid state owing to the compression of the molecule. We thus only specify the possibility of a yet further change of the same sort, which finally produces a new equilibrium between  $\eta$  and  $v$  in the solid state. Beforehand there can be no question of explaining the solid state by referring it to the same processes as those which exist in the liquid state. This can only be done when the relation of the elasticity for instantaneous changes of volume and the time of relaxation for the liquid and solid states are worked out

1) We use the  $a$  and  $b$  of VAN DER WAALS in the most general manner given by this physicist.

and the great change of the time of relaxation with the above mentioned further change of  $b$  at the transformation from solid to liquid is explained on the same grounds. Still keeping this in view we may say that by prolonging the line  $hi$  till it reaches the solid state we have given what VAN DER WAALS calls the equation of state of the molecule.

Now it follows immediately from this representation that the form of the connecting line  $hi$  must be taken as dependent upon the temperature and the inflection as decreasing and finally vanishing with rising temperature. Thus the above consideration of the form of the liquid ridge on the GIBBS' surface necessitates the assumption that the solid can be joined to the liquid ridge by a plait. This will be generally perpendicular to the  $v$ -axis and will end in a plaitpoint i.e. this indicates the continuity of the gaseous and solid states of aggregation.

With these considerations we have not treated the question whether the conditions in the plait which we assume to exist in the gap between the two states of aggregation (c.f. § 2 for outside the plait) are also conditions of *equilibrium*, *labile* or otherwise. We have advanced no reason for this. This is as far as we know not done by others either who have assumed the existence of similar conditions<sup>1)</sup>. In considering the vapour, we stated that there have not been observed metastable states connecting the solid with the gaseous and liquid states. However these appear very clearly and markedly between the gaseous and liquid states, and have an important bearing in the theory of VAN DER WAALS.

Also it is not unlikely that VAN DER WAALS has never in his writings treated the continuity of the gaseous and solid states, and has expressly kept it in the background, because the use of such intermediate states as those above considered is only allowed theoretically when it is shown — as VAN DER WAALS did for the intermediate vapour-liquid states — that these intermediate states may be treated as conditions of equilibrium. However we do not propose to determine “the molecular equation of state” from a given mechanism, but to seek for an empirical form for this from the known facts by induction. In this case we must use the most obvious analogies as indications and it is not allowed to deviate from the most simple suppositions without proving each step. With variable molecules it is probable that relations between entropy and volume can exist other than those which VAN DER WAALS has already treated in his equation of state based on the theory of cyclic motion. In order

<sup>1)</sup> See especially OSTWALD, Textbook of general chemistry.

to be able to fix a meaning for some of the conditions which according to this possibility are suggested by us, we must suppose that the material can suffer stresses with imponderable as well as with ponderable mechanism. Thus we may obtain actual values for  $\eta$  as well as for  $v$  at which we can keep the material homogeneous which in reality would be impossible. No difficulty should arise if we in addition to general assumptions suppose that the entropy can be kept constant. We only extend to the imponderable mechanism what is generally allowed for the ponderable, when one supposes the substance kept homogeneous with constant volume in VAN DER WAALS labile conditions.

We have thus in the following set ourselves to model the parts of the GIBBS' surface which are experimentally known, for substances which exist in the solid state, to add to these portions the vapour and liquid regions following VAN DER WAALS, and to combine the region thus obtained with the solid ridge in such a manner that the isotherms on the GIBBS' surface shall differ as little as possible from the *unchanged* isotherm of VAN DER WAALS, and the *course of the isotherm in the  $\eta v$  projection shall be as simple as possible*. We have e. g. excluded states on the surface where  $T = 0$  except at  $\eta = -\infty$  and have supposed that for every value of  $\eta$  and  $v$  only one value of  $\varepsilon$  belongs.

It is clear that the problem formulated thus does not extend further than the search for a continuous function, which for a known range coincides with the GIBBS' surface and satisfies a given — but physically we hope happily chosen — criterion of simplicity. The solution obtained from this determination has a certain value and forms a continuation of the investigation of Comm. Nos. 71 and 74<sup>1)</sup>, the development of the equation of state in series.

There also the principal object was to produce a numerically correct combination of the experiments independent of the thermodynamic peculiarities of the substances treated. The solid state was at first not considered in order to avoid a too large field. With this limitation it appeared that the whole range of experiment for normal substances could be expressed by a series condensed to a polynomial in powers of  $\frac{1}{v}$ , so that we could find exact values for  $p$ , for  $\eta = \int \frac{dp}{dt} dv$ , for  $\varepsilon = \int \left( T \frac{dp}{dt} - p \right)$  (and other quantities e. g.  $\psi = - \int p dv$ ) for all states within the region considered, without tedious calculations.

<sup>1)</sup> KAMERLINGH ONNES. Ueber die Reihenentwicklung für die Zustandsgleichung der Gase und Flüssigkeiten, Livre jubil. Bosscha Archives Néerl. (II) T. VI p. 874—888, '01. Leiden Comm. n<sup>o</sup>. 74.

The extension of this idea to associated substances was necessarily excluded since the law of corresponding states was taken as the basis of the development. The existence of a maximum density for water need then bring no difficulty for the representation of the liquid state in the consideration that in general  $p$ , and thus  $\eta$  also, is given along an isotherm by powers of  $\frac{1}{v}$ . The question, if the connection between  $\eta$  and  $v$ , which follows from the mechanism of the liquid or gaseous states, can *in general* be given by expressing  $\eta$  in powers of  $\frac{1}{v}$ , could be left out of account. Now that we wish to introduce the solid state into the polynomial — until now not used, but after some change perhaps applicable for this purpose — we meet the difficulty that with many substances solidification is accompanied with increase of volume. For water, which falls in this case, the question is treated more fully in §§ 3 and 4. Still if this case could not, as we have supposed, be explained by association, and if in general the complete knowledge of the mechanism of the solid state for the isotherms of gas, liquid and solid leads to an implicit relation between  $\eta$  and  $v$ , still for one part of the range of  $\eta$  it will be possible to express this directly by one value in terms of  $v$ . It appears to us to be quite possible that with certain normal substances  $p$  can be empirically expressed in powers of  $\frac{1}{v}$  over the whole range under consideration.

The GIBBS' surface, which we have constructed for this first class of substances, will serve to give not improbable corresponding values of  $p$  and  $v$  for an isotherm in the liquid-solid plait, and to permit computation of useful values for the virial coefficients — the coefficients in a polynomial

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \dots$$

If we seek for the values which these coefficients can have, we find a second connection between this investigation and Comms Nos. 71 and 74. In both of these it is shown that values will be found for the reduced virial coefficients of different substances, which are sufficiently, but still not quite, equal. These differences in  $\mathfrak{B}$   $\mathfrak{C}$  etc. will just give the deviations of the various substances from the law of corresponding states. They express parts of the molecular interaction which cannot be explained or represented by the actions of homologous points which last actions are those whose mechanical

similarity results in the law of corresponding states. The various substances certainly differ widely in the solid state when they are expressed with reduced coefficients. Thus the mechanical dissimilarity of the actions of unhomologous points appears at once. When the same isotherm passes through the gaseous liquid and solid states, the higher coefficients of the polynomium must without doubt differ considerably. It is thus to be expected that the lower coefficients, will also exhibit certain but smaller differences, which are connected with those in the higher coefficients. In this manner, in the comparison of two substances, the deviations from the law of corresponding states would be clearly connected with the solid properties of the two given substances.

Further, as the virial coefficients give the deviations from the BOYLE GAY-LUSSAC law we may say that these deviations do not only express the properties of the liquid state as given by VAN DER WAALS but also those of the solid state. Really a connection between the deviations and the properties of the solid state is also implied in VAN DER WAALS' last development of the equation of state after the method of cyclic motion.

§ 2. The best possible connection of the known part of the solid with the liquid ridge by a continuous surface has some similarity with the use of the continuous line by which J. THOMSON connected the liquid and gaseous states found by ANDREWS. Still there remains a marked difference. THOMSON could start from the existence of a critical point. A continuous change from the solid to the liquid state is not experimentally proved, it is doubted by some and as to the crystalline modification it is directly contradicted by TAMMANN. If TAMMANN's theoretical considerations were correct, then it would already be clear that we had produced only a simple empirical interpolation when we intended to have constructed a group of intermediate states which beforehand would be at least probable on physical grounds.

TAMMANN's objections are certainly not conclusive. They rest in the same way as our assumptions on extrapolations outside the experimental region, and it appears that our extrapolation is more probable than his. Also TAMMANN's combination of the fusionline of water, an associating substance, with that of other substances as if they were two cases which could pass one into the other by change of temperature and pressure, presents some important difficulties. We have not to consider these conclusions so long as we exclude associated substances and substances of perhaps very complicated character. Instead of giving immediately a general treatment of cases so

different in principle, we confine ourselves to the simplest group of substances.

For these we have constructed the representation which we shall further develop in the following.

In agreement with TAMMANN, we also assume, although undercooling only occurs to a limited extent, that the liquid ridge continues to very low temperatures (at first we may assume to the absolute zero) states with increasing times of relaxation up to the glass condition being encountered in passing over the ridge towards decreasing temperature. Thus we do not come into collision with the observations. Still we do not mean that it is quite impossible for crystalline properties to be found on the glassy ridge e.g. at very low temperatures. Further we do not suppose that the existence of one such a ridge would exclude the possibility of other amorphous conditions where other equilibrium relations between entropy and volume could equally be found. Moreover it is highly doubtful if the term amorphous does not include very various structures in the solid state, so that it is certainly not necessary that an amorphous condition should be present on the ridge where liquid would be found at a higher temperature. As to the crystalline ridge, our whole representation makes it appear more probable to us, that the crystalline ridge in the simplest case should run next to the liquid ridge down to very low temperatures, than that it should follow TAMMANN's ring shaped form (c. f. § 4).

The process of transformation from the crystalline to the gaseous (below the liquid-gas critical temperature, liquid) state does not at all disagree with the usual assumptions concerning the molecular forces, but is immediately to be deduced from them. A very satisfactory agreement with the suppositions would be obtained when the characteristic difference between two ridges appeared to result from the differences of density and entropy (specific heat) of the modifications, the crystalline or amorphous form taken by each of these modifications being thermodynamically of secondary importance, so that for a first investigation they would not come into account in comparison with the change of properties of the solid phase due to differences of density and entropy.

However it may be, we must certainly assume that the crystalline form will result from the molecules being by choice oriented and arranged in a given manner owing to the forces from the not corresponding points. The directing and arranging forces will then be different for different densities and entropies, whence the most probably occurring orientation and arrangement will be different

for different densities and entropies and the crystal form will be different for various modifications.

The increase of the vibration energy will gradually efface the mean predominant most probable distribution and orientation as the crystal is raised in temperature and although the whole continually approaches a uniform mean distribution and orientation still some different groups will remain in arrangements of most probable predominant distribution and orientation. In particular if this hypothesis is applied to the case of a gaseous and a solid phase in equilibrium which are brought together to a higher temperature, fresh hypotheses must be made to render it clear that no identity of the two phases can become possible and therefore no continuity of solid and gaseous states will be found. Of course it does not matter if the temperature under consideration is above the liquid-gas critical point. Further there is no reason known why it should not be allowed to extend the double convex part of the GIBBS' surface, — containing essentially states of equilibrium, to higher temperatures and pressures, so that it surrounds the critical point at the end of the plait.

It is quite in harmony with our assumptions of § 1 that, in the gaseous phase of a substance occurring also as solid, molecular groups will at all times be found (produced always from different individuals) in which the particular attraction between not equivalent points<sup>1)</sup>, predominating in the solid state, will also be manifest. Below a certain temperature it will then be necessary to momentarily consider certain portions of the gas as crystalline. We are here only following the method employed by BOLTZMANN for the determination of the equilibrium distribution, which is the most probable. We apply it to a given density and velocity distribution but also extend it to orientation and arrangement.

We have mentioned above the existence of more ridges which appear successively on the GIBBS' surface towards the side of diminishing volume. This case appears to us to be the normal one. It is probable that the various solid modifications are not known for most substances. If we further consider that a small change in the course of the isotherms can cause one ridge to rise above another and thus to represent more stable phases or not, it is not at all probable that just those modifications of the various substances are known, which belong to corresponding ridges. It is therefore, possible that in the solid state the various substances would differ less than now appears to be the case if one were acquainted with all their modifications; finally the

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<sup>1)</sup> Comp. REINGANUM, *Drudes Annalen*. 1903. 10 p. 334.

possibility remains that more liquid ridges could exist along which with falling temperature the time of relaxation would not increase to the value required for the solid state, while states of equilibrium between the two are to be expected, so that the same substance could exist in two liquid modifications.

The reasons why such a case is not known and why the various solid modifications are usually crystalline, must be further explained by a theory of the solid state.

§ 3. Following the lines developed we have constructed three models of GIBBS' surfaces.

We have first considered an imaginary substance, which partially corresponds with carbon dioxide, in the liquid state is in harmony with VAN DER WAALS' original equation, and which further can exist in one solid (crystalline) modification. For the GIBBS' surface of this substance constructed according to our ideas, we have only considered that portion where the fusion line of the substance is to be found. This model serves principally to present clearly the views on the solid state advanced in this communication.

Having assumed that we can express the character of the peculiarities in the transition from solid to liquid by this model, we have further constructed two others, which refer to the actual  $\text{CO}_2$ , and on which all known thermodynamical properties are expressed as numerically exact as possible.

One of the models represents the whole surface for  $\text{CO}_2$ , with the exception of the portions for the ideal gas state and for very low temperatures.

The second gives, on a necessarily larger scale, the region where the transition occurs between the various modifications with small volumes.

Finally another model has been formed which demonstrates sufficiently, that taking it in general, a substance like water can be represented in the manner followed by us. We mean that the deviations which this substance exhibits can be brought into line with the association. In general a liquid ridge which corresponded sufficiently with the VAN DER WAALS equation of state, would be pressed upwards and towards decreasing volume by the association. This transformation is represented schematically in the  $\eta v$  projection by fig. 5. To the right lies the undisturbed VAN DER WAALS ridge, given by the portion where the connodal liquid-vapour, the curve drawn, runs to the left, the twisted ridge is again given by the



Fig. 5.

altered portion, the two portions of the connodal solid-vapour are again drawn (unfortunately the altered connection is omitted in the figure). At  $m$  lies the maximum density of water under its own vapour pressure. The preliminary model made by us serves to show, that the most notable properties of  $H_2O$  will be correctly given if we consider the ice ridge as an ordinary solid ridge on the surface, and the liquid ridge as changed by the last mentioned process owing to the association.

We hope shortly to obtain models which will exhibit the transformation of the different modifications or allotropic states as well as the peculiarities of the expansion phenomena. In this way we hope to contribute to a somewhat better insight, at least to a better survey, of the thermodynamical character of the different substances. However in addition to the questions relating to association there are others, which have reference to mixtures, saturated solutions etc., and which would necessitate a long investigation. We hence think that the results now obtained from a sufficiently independent whole to be published.

We have thus in the above made the meaning of our work clear and can now proceed to describe the models somewhat more fully and to show that the experimental data can really be obtained on these surfaces.

#### I. THE SOLID-LIQUID PLAINT ON THE GIBBS' SURFACE.

*(Representation of the continuity of the solid and gaseous states).*

The specific heat of the imaginary substance in the gaseous state has been assumed to be equal to half that of liquid carbon dioxide: the specific heat in the solid state as equal to that which is found by employing NEUMANN'S law. Also the substance obeys the VAN DER WAALS equation of state for carbon dioxide in the liquid and gaseous states. It appeared useful to give for this model (pl. II, fig. 1) front and side elevations and plan (pl. III fig. 1, 2, 3, 4) with the lines  $\eta = \text{const.}$ ,  $v = \text{const.}$ ,  $T = \text{const.}$  (dashed lines)  $p = \text{const.}$  (dotted lines), for which the drawings are sufficiently explanatory. The connodal fluid (gas)-solid is drawn on this model and the coexisting states joined by steel wires.

The principal difference between our representation and TAMMANN'S is very clearly seen on comparing the plan (pl. III fig. 2) with his figure (DRUDE'S Ann. 3 p. 190).

This model is also useful for a comparison of our idea with the well known scheme given by MAXWELL (Theory of Heat, p. 207)

our plan is easily compared with the latter for the small volume part. To find how our vapour plait will be connected with this portion, it is only necessary to use pl. III fig. 2. The chief difference is seen in the different forms of the spinodal line. Ours is given by the dot-dash line of fig. 6 and MAXWELL'S in fig. 7. Ours consists of two portions which remain apart to the lowest temperature



Fig. 6.

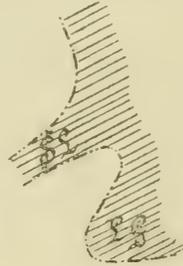


Fig. 7.

( $T = 0$ ), while MAXWELL'S shows only a secondary loop. Quite improbable are MAXWELL'S isotherms. They show in the vapour plait a point of inflection in the isotherms. Thereby they differ entirely from the equation of state of VAN DER WAALS, which is certainly qualitatively correct for vapour and liquid.

II. THE GIBBS' SURFACE FOR CO<sub>2</sub>.

(The general model).

This model was constructed by the help of the empirical equation of state given in Comms. Nos. 71 and 74 with the assistance of the thermodynamical formulæ obtained in No. 66.

$$\begin{aligned} \varepsilon_r T - \varepsilon_K &= \int_{T_k}^T c_v dT + \int_{c_k}^v \left( T \frac{dp}{dT} - p \right) dv + \int_v^c \left( T \frac{dp}{dT} - p \right) dT \\ \eta_{ir} T - \eta_{ik} &= \int_{T_k}^T c_v dT + \int_{c_k}^v \left( \frac{dp}{dT} \right) dv + \int_v^c \left( \frac{dp}{dT} \right) dT \end{aligned}$$

whence

$$\begin{aligned} \varepsilon &= c_v (T - T_k) - p_k v_k \frac{b_2 + 2b_3 + 4b_4}{\lambda^2} - \frac{p_k v_k}{2} \frac{c_2 + 2c_3 + 4c_4}{\lambda^3} \\ &- \frac{p_k v_k}{4} \frac{b_2 + 2b_3 + 4b_4}{\lambda^5} + \frac{p_k v_k^2}{v} \frac{b_2 + 2\frac{b_3}{t} + 4\frac{b_4}{t^3}}{\lambda^2} + \\ &+ \frac{p_k v_k^3}{2v^2} \frac{c_2 + 2\frac{c_3}{t} + 4\frac{c_4}{t^3}}{\lambda^3} \dots \dots \dots (1) \end{aligned}$$

$$\begin{aligned}
 \eta = & c_v l \frac{T}{T_k} + \frac{p_k v_k A_0 \alpha l v}{T_k \lambda v_k} + \frac{p_k v_k}{T_k} \frac{t_1 - t_3 - 3 t_4}{\lambda^2} + \\
 & + \frac{p_k v_k}{2 T_k} \frac{c_1 - c_3 - 3 c_4}{\lambda^3} + \frac{p_k v_k}{4 T_k} \frac{v_1 - v_3 - 3 v_4}{\lambda^5} \\
 & - \frac{p_k v_k^2}{T_k v} \frac{t_1 - t_3 \frac{1}{t} - 3 \frac{t_4}{t^3}}{\lambda^2} - \frac{p_k v_k^3}{2 T_k v^2} \frac{c_1 - \frac{c_3}{t} - \frac{3 c_4}{t^3}}{\lambda^3} \quad (2)
 \end{aligned}$$

As specific heat  $c_v$  in the ideal gas state we have taken  $0,17419 \cdot 10^5 = 71,2 \times 10^5$  1), and it is considered constant. For the critical constants we have used

$$T_k = 304,5^\circ, p_k = 73.1014 \cdot 10^3 = 740 \cdot 10^5 \frac{gr}{cm \text{ sec}^2}$$

from the experiments of AMAGAT and

$$v_{yk} = 2.20 \frac{cm}{gr} \text{ from the experiments of KUENEN and ROBSON } 2)$$

deduced by the law of the rectilinear diameter.

The assumed critical values give:

$$\lambda = 0,001044.$$

With (1) and (2) have been calculated

a) five points belonging to the ideal gas state, where  $v_y$  is taken as 180:

1. for $t = 0.40$	$v_y = 180$ $\eta = 43,1 \times 10^5$ $\varepsilon = 300 \times 10^7$
2. for $t = 0.60$	$v_y = 180$ $\eta = 71,8 \times 10^5$ $\varepsilon = 46 \times 10^7$
3. for $t = 0.68$	$v_y = 180$ $\eta = 81 \times 10^5$ $\varepsilon = 64 \times 10^7$
4. for $t = 1$	$v_y = 180$ $\eta = 108 \times 10^5$ $\varepsilon = 133 \times 10^7$
5. for $t = 1,18$	$v_y = 180$ $\eta = 120 \times 10^5$ $\varepsilon = 173 \times 10^7$

b) two points on the gaseous branch of the connodal line for which KUENEN and ROBSON (loc cit) have given the values of  $T$  and  $v$

1) Sufficiently near the value given by REGNAULT.

2) KUENEN and ROBSON, Phil. Mag. 6 p. 149, 1902.

6. for $t = 0.714$	$v_y = 74$
	$\eta = 65 \times 10^5$
	$\varepsilon = 61 \times 10^7$
7. for $t = 0.68$	$v_y = 113$
	$\eta = 70 \times 10^5$
	$\varepsilon = 57 \times 10^7$

The first of these belong to the triple-point gas-liquid-solid.

c.) The points of the liquid state belonging to 6 and 7 are calculated with the help of KUENEN and ROBSON's numbers for the heat of vaporisation. We have found

8. for $t = 0.714$	$v_y = 0,85$
	$\eta = -102 \times 10^5$
	$\varepsilon = -262 \times 10^7$
9. for $t = 0.68$	$v_y = 0,83$
	$\eta = -122 \times 10^5$
	$\varepsilon = -304 \times 10^7$

In the same way taking into account the heat of fusion at the triple point we find for a point belonging to the solid state.

10. for $t = 0,714$	$v_y = 0,68$
	$\eta = -187 \times 10^5$
	$\varepsilon = -446 \times 10^7$

The model (see Pl. II fig. 2) is constructed with

the values of $v$ in cms	$= \frac{1}{3}$	of the above numerical values
" " " $\eta$ " "	$= \frac{1}{10^6}$	" " " " "
" " " $\varepsilon$ " "	$= \frac{1}{2 \cdot 10^8}$	" " " " "

According to TAMMANN two solid modifications of  $\text{CO}_2$  exist so that we must add two solid ridges (see Pl. II fig. 2) in addition to the liquid ridge. We have assumed that TAMMANN's 2<sup>nd</sup> modification lies between the fluid state and the first modification, and we call TAMMANN's 2<sup>nd</sup> modification  $A$  and his first  $B$ . The reason why we have assumed this arrangement between the two solid modifications is the following : TAMMANN<sup>1)</sup> has determined the fusion line for the modification  $A$  as well as for  $B$ , and also the transition line for the second modification.

He found (see Pl. I fig. 1) that the values of  $\frac{dp}{dt}$  are greatest for the points on the equilibrium line  $c$ , smallest for the fusion line  $a$  of the modification  $A$  and found between the two another locus for the fusion line of the modification  $B$ . The same is also to be obtained from our

<sup>1)</sup> TAMMANN, Ann. Phys. u. Chemie 1899 Bd. 68 pg. 553.

model with the position of the ridges chosen, while it is at the same time easy to see that by another arrangement the  $\frac{dp}{dt}$  for the three lines will not agree so well either with TAMMANN's values or with our desire to make the course of the temperature line the simplest possible. We hence consider that the arrangement of the ridges which we have chosen agrees with the experiments and that thus the specific volume of the modification *A* is larger than that of *B*.

On this model the binodal for the liquid and gaseous condition (line *GL*) is shown and also the gas branch of the binodal for the gaseous state and the modification *B* (line *GL<sub>B</sub>*). The three points belonging to the triple-point gas-liquid-solid *B* are joined two and two by steel wires. The dashed line which passes through these points is the isotherm of the triple-point, and close to this runs the critical isotherm. The dotted line is the pressure line of the triple-point. According to TAMMANN's values the solid phase of this triple-point belongs to the modification *B*, while the ridge of the *A* modification (see Pl. III fig. 5) lies below the fundamental plane of the triple-point determined by KUENEN and ROBSON. A tangent plane that touches at more than three points, cannot be placed on our model which is in agreement with the phase rule. In addition to the just mentioned triple-point the existence of two others on our model, the triple-point gas-liquid-solid *A* and the triple-point liquid with the two solid modifications *A* and *B* is rendered probable by TAMMANN's experiments.

On comparing our model with one constructed after the equation of VAN DER WAALS, one sees that on ours the liquid ridge rises more steeply from the critical temperature to the lower temperatures. It hence follows that the specific heat of the liquid is too small on the model after VAN DER WAALS. The slow rise of the liquid ridge in the latter has also the result that the heat of vaporisation is too small.

### III. THE GIBBS' SURFACE FOR CO<sub>2</sub> AT GREATER DENSITIES.

*(Detail model of the liquid and solid states).*

For the general model the specific heat at constant volume was assumed to be constant in the ideal gas state. But for the construction of the detail model, to be now described, we have been obliged to consider the variability of  $c_v$ . REGNAULT and E. WIEDEMANN have measured  $c_p$  for CO<sub>2</sub> at one atmosphere pressure and various temperatures, and have expressed the change with *T* by empirical formulae.

The results of the two investigators agree well. If one seeks from the empirical equation of state for 0° C. the correction which must be made on  $c_p$  at one atmosphere to reduce it to the ideal state, one finds 0.003 cal., which quantity lies within the limit of experimental error. The correction is still smaller for higher temperatures. We also find that the correction, which is necessary to reduce the specific heat  $c_p$  of aether found by E. WIEDEMANN to the ideal state, is too small to come into account. The formulae given by REGNAULT and E. WIEDEMANN for the specific heat of gases and vapours are thus applicable to the ideal state at least with close approximation. Hence LEDUC's contention<sup>1)</sup> is refuted that for substances which obey to the law of corresponding states both  $c_p$  and  $c_v$  are constant in the ideal gas state. From the experimental values of  $c_p$  and the well known relation  $c_p - c_v = \frac{R}{m}$ , we can calculate the value of  $c_v$  and its variation with the temperature.

Having found  $c_v$  in this manner we calculated the corrections which must be made to the equations (1) and (2) due to the variation of  $c_v$ . We find the following new values for the points on the liquid branch at  $t = 0.714$  and  $t = 0.68$  and for the solid phase at the triple-point

points of the liquid state

$$\begin{aligned} \text{I. for } t = 0,68 \quad v &= 0,83 \\ \eta &= -117 \times 10^6 \\ \varepsilon &= -286 \times 10^7 \end{aligned}$$

$$\begin{aligned} \text{II. for } t = 0,714 \quad v &= 0,85 \\ \eta &= -96 \times 10^6 \\ \varepsilon &= -245 \times 10^7 \end{aligned}$$

point of the solid state

$$\begin{aligned} \text{III. for } t = 0,714 \quad v &= 0,676 \\ \eta &= -180 \times 10^6 \\ \varepsilon &= -420 \times 10^7 \end{aligned}$$

Now we must investigate the liquid range for higher pressures more exactly and in the first place determine  $c_v$ . This follows from the formula

$$c_p - c_v = T \int_v^x \frac{\partial^2 p}{\partial T^2} dx$$

<sup>1)</sup> LEDUC, Recherches sur les gaz. Paris 1898 and 99.

by introducing the value of  $p$  from the empirical equation of state, this gives

$$c_v - c_V = \frac{T v_k p k}{T_k^2} \left\{ - \frac{d^2 \mathfrak{B}}{dt^2} \frac{v_k^2}{\lambda^2 v^2} - \frac{1}{2} \frac{d^2 \mathfrak{C}}{dt^2} \left( \frac{v_k}{\lambda v} \right)^3 - \frac{1}{4} \frac{d^2 \mathfrak{D}}{dt^2} \left( \frac{v_k}{\lambda v} \right)^5 - \right. \\ \left. - \frac{1}{6} \frac{d^2 \mathfrak{E}}{dt^2} \left( \frac{v_k}{\lambda v} \right)^7 - \frac{1}{8} \frac{d^2 \mathfrak{F}}{dt^2} \left( \frac{v_k}{\lambda v} \right)^9 \right\};$$

for  $t = 0.897$  or  $T = 273$  and  $v = 1.020$  we find

$$c_v - c_V = 0.0432$$

or, since at  $T = 273$   $c_V = 0.1431$  is

$$c_v = 0.1863$$

The point corresponding to  $v = 1.02$  and  $t = 1$  in the liquid region is now found. This was obtained by the aid of the equations 1) and 2) where the term  $\mathfrak{D}$  must be certainly taken into account; we find

$$\text{IV. for } t = 1 \quad v_y = 1.020 \\ \eta = \eta_{T_{kv}} = - 42.10 \times 10^5 \\ \varepsilon = \varepsilon_{T_{kv}} = - 115 \times 10^7$$

If we now assume that at the same temperature the difference between the specific heats at constant volume in the ideal gas state and for the volume 1.020, is constant and equal to  $k$ , we have

$$\varepsilon - \varepsilon_{T_{kv}} = \int_{T_k}^T c_P dT - \left( \frac{R}{m} + k \right) (T - T_k), \\ \eta - \eta_{T_{kv}} = \int_{T_k}^T \frac{c_P}{T} dT - \left( \frac{R}{m} + k \right) l \left( \frac{T}{T_k} \right),$$

with which the following points for  $v = 1.020$  are calculated:

$$\text{V. for } t = 0.864 \quad v_y = 1.020 \\ \eta = - 53.6 \times 10^5 \\ \varepsilon = - 145 \times 10^7$$

$$\text{VI. for } t = 1.314 \quad v_y = 1.020 \\ \eta = - 28 \times 10^5 \\ \varepsilon = - 33 \times 10^7$$

According to the numbers of KUENEN and ROBSON the first of these two points lies on the liquid branch of the binodal line.

The model Pl. II fig. 3 is constructed from the values for these points.

The values of $v$ used are	100	times the calculated
.. .. . $\eta$ .. ..	$2 \times 10^{-5}$	.. .. .
.. .. . $\varepsilon$ .. ..	$10^{-8}$	.. .. .

Further, care has been taken to give the tangent plane the proper inclination at these points in agreement with

$p = - \left( \frac{\partial \varepsilon}{\partial v} \right)_{\eta}$  ,  $T = \left( \frac{\partial \varepsilon}{\partial \eta} \right)_{v}$ , so that temperature and pressure shall have their real value.

On the given drawings (scale  $1/4$  of model) for plan and elevation Pl. III, fig. 5 and 6 — one side elevation has been rejected as it does not clearly show the course of the pressure and temperature line — the behaviour of the line  $T = \text{const}$ ,  $p = \text{const}$ ,  $v = \text{const}$ ,  $\eta = \text{const}$  and the position of the triple point can be seen without further explanation. We draw attention to the intersection of the connodal line  $S_A S_B$  by the connodal line  $S_L S_B$  and further to the passage of the isotherms over the connodal line and the crossing of the isotherms with their corresponding isopiestic. In order to read from the isotherms, given on the model, the corresponding values of  $p$  and  $v$ , the diagram of the isotherms (see Pl. I, fig. 2) was constructed, which reminds one of the course of the isotherms derived from the VAN DER WAALS' equation. The point  $Z_1$  in this figure corresponds to the triple point for liquid and the two solid modifications of carbon dioxide. According to TAMMANN the pressure is 2800 K.G. The point  $KL S_a$  is the critical point of the modification  $A$  in the fusion line. According to the model the critical pressure would be 6500 K.G. and the reduced temperature 1.7,

The critical point  $GL$  occurs so far to the right on this scale (the unit of volume is equal to that of Pl. III fig. 5 and 6) that it cannot be represented in the drawing.

*No critical point exists* for the transition of  $S_B$  to  $L$  owing to the interposition of the ridge  $S_A$ . The binodal line on  $S_B$  and  $L$ , loses its physical meaning at a given position of the rolling tangent plane. A continuous passage from  $S_B$  to  $S_L$  is only possible through the gaseous as an intermediate state.

An important result can be obtained from the foregoing. Whenever substances exist whose molecules undergo changes in the transition to the solid state, which are mechanically similar to those which determine the condition of the two phases, these said substances will also agree with the law of corresponding states in the solid condition. An experimental investigation for the continuity of the solid and gaseous states would be best made on the substance with the lowest critical pressure. If, for the moment, we assume that  $H_2$  and  $CO_2$  are sufficiently comparable from this point of view — at present no better example is at hand — the critical point solid-gas should be sought at about 1800 atm. and  $-210^\circ C.$ , and thus in possible

experimental pressure and temperature ranges. For many years a similar investigation has stood on the program of the Leiden Laboratory.

IV. THE GIBBS' SURFACE FOR  $H_2O$  FOR GREAT DENSITIES.  
(*Model for the equilibrium of TAMMANN'S ice varieties and water*).

The GIBBS' surface suffers a deformation from association in the case of water, and the general character of the change has been already given in § 3 according to our views. Having once arrived at a given idea about the general form, we can more exactly determine the form to be ascribed to the ridges according to this idea by the help of the experimental numbers. The model that we have obtained by our method is shown on Pl. II fig. 4. As TAMMANN has already indicated, two other ice varieties (ice II and ice III) are found, in addition to ordinary ice (ice I). The general position of the ridges belonging to these values follows from TAMMANN'S measurements concerning the volume change and heat of transformation for the transition of one ice variety into another or into water. If we give the value 0 to the last and 1, 2 and 3 to the three ice varieties, TAMMANN finds at  $T = 251$  (triplepoint water — ice I — ice III)

$$\begin{aligned}\Delta v_{01} &= 0.14 \\ \Delta v_{03} &= -0.05 \\ \Delta v_{31} &= +0.193 \\ r_{01} &= -73 \text{ cal.} \\ r_{03} &= -70 \text{ " } \\ r_{12} &= +3 \text{ " }\end{aligned}$$

Also TAMMANN finds that  $\Delta v_{12}$  is very nearly equal to  $\Delta v_{13}$ . We have assumed that  $\Delta v_{21}$  is somewhat greater than  $\Delta v_{31}$ . We then find the general arrangement given in Pl. IV fig. 1 for the water and three ice varieties. The dashed line gives the isotherm through the triple point water — ice I — ice III, the dotted line the isopiestic. We have not taken these from pl. II, fig. 4, where no isotherms or isopiestic are drawn, because this figure is not sufficiently worked out for this purpose. We have drawn on Pl. IV. schematic figures in order that they may be used in continual comparison with the surface, whenever we wish to further explain the properties of the surface. From these we can show easily that they agree with the model of Pl. II, fig. 4.

We now further specify our ideas for the modification 0 and 1. Here  $\frac{dp}{dt}$  is negative for points on the binodal line, and this also

follows from the model. In fig. 2 Pl. IV, let  $AA'$  and  $BB'$  be a pair of coexisting phases. A higher temperature belongs to  $AA'$  than to  $BB'$ , while the pressure at  $AA'$  is greater than that at  $BB'$ . If we extend the fusion line of ice in the direction of falling pressure, it is probable that for a given negative value of  $p$ ,  $\frac{dp}{dt}$  would change

its sign and become positive. Those phases for which  $\frac{dp}{dt} > 0$  would

be determined by  $DD'$ ,  $EE'$  and  $FF'$ . The critical point water-ice I would be found at  $G$  and would therefore present a negative value. POYNTING<sup>1)</sup> came to the same conclusion in a different way. A second critical point at positive pressure, which is deduced by POYNTING and also by PLANCK<sup>2)</sup> by linear extrapolation of the variation of the latent heat of fusion, which is also given by us, becomes impossible by the appearing of the other ice varieties, which we will describe now. If we assume, returning to  $AA'$ , that by rolling the common tangent plane to  $CC$  in the direction towards  $BB'$  on the water and ice I ridge, we should also touch the ridge ice III at  $H'$ . Then  $\frac{dp}{dt}$  would be positive for water and ice III, in agreement

with TAMMANN's measurements. If now we suppose that ice III is non-existent, we may prolong the binodal line  $AC A' C'$  to a little over  $CC'$  which gives us continually lower temperatures and higher pressures. For a given position the tangent plane will now also touch the ice II ridge. Hence we obtain a lower temperature  $T_2$  for this triple point than for the triple point water — ice I — ice III, while the pressure is higher for  $T_2$  than for  $T_1$ . This is also in agreement with TAMMANN's results. In the same way for water — ice III and water — ice II is  $\frac{dp}{dt} > 0$ .

According to our model the fusion curve of ice II has a termination at higher pressures and temperatures and therefore we have assumed that a critical point water — ice II exists.

Now we consider further the transformation line ice I to ice III. According to TAMMANN the heat of transformation from ice I to ice III is positive in the neighbourhood of the critical point  $T = 251^\circ$  and at lower temperatures negative. In order to be in agreement with this, the ice I ridge has been given a strong curvature and the ice III ridge a weak (see fig. 3 Pl. IV where the elevation of the ridges from the side of the  $\eta\varepsilon$  plane is shown). Hence the course of the

<sup>1)</sup> POYNTING Phil. Mag. (5). 12. 1881.

<sup>2)</sup> PLANCK. Wied. Ann. Bd. 15 p. 460. 1882.

H. KAMERLINGH ONNES and H HAPPEL „The representation of the continuity of the liquid and gaseous conditions on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of Gibbs. Pl. 1.

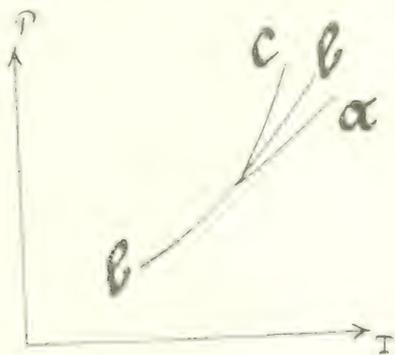


fig. 1

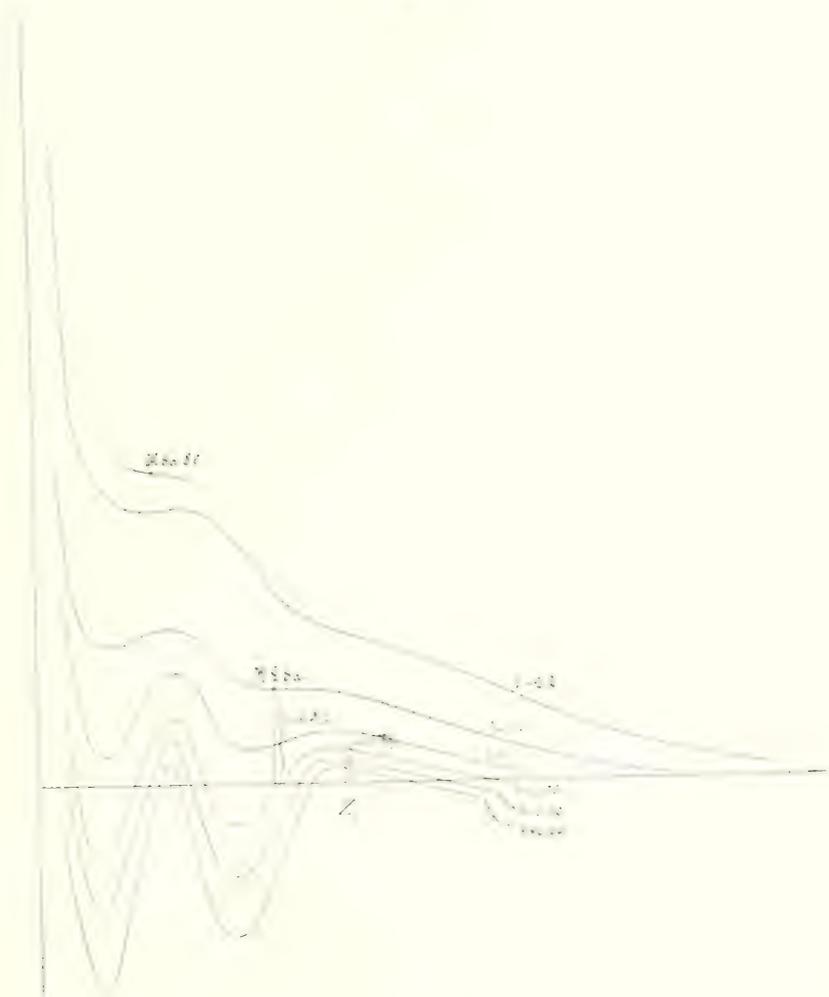


fig. 2



binodal curve is given by the line drawn in fig. 4 Pl. IV. It is easy to see that now  $\frac{dp}{dt} < 0$  at the triple point  $251^\circ$  and  $\frac{dp}{dt} > 0$  at lower temperatures. The transformation line has thus the course drawn in fig. 5 Pl. IV, which qualitatively is in complete agreement with TAMMANN's determinations for this line.

The transformation line from ice I to ice II is very similar to that from ice I to ice III. Since the ice II ridge distinctly rises more steeply than the ice III ridge the line of transformation from ice I to ice II is more curved than that for ice I to ice III. The result is that the line of transformation from ice I to ice II cuts, above the absolute zero, the vapour pressure line of ice I, which runs very close to the  $T$ -axis (see fig. 6 Pl. IV). A triple point vapour — ice I — ice II corresponds with this common point, this has not been observed, but TAMMANN holds its existence as probable. Also the transformation curve from ice I to ice III (Pl. IV fig. 5) when produced cuts the  $T$ -axis. The common point then corresponds to a negative temperature, and thus this triple point cannot be realised.

The curve of transformation from ice II to ice III was not determined by TAMMANN, but its course can be seen on our model.

From the model it follows that TAMMANN could obtain ice II by cooling to  $-80^\circ$  C., while less cooling would be sufficient for ice III.

Owing to the form which we have chosen for the liquid ridge, the expansion coefficient of water near  $0^\circ$  C. would be negative and water would show a maximum density, while the expansion coefficient of ice would be positive, all in agreement with experiment. The pressure lines for water (see fig. 7 Pl. IV) run in accordance with this (at least near  $0^\circ$ ) from larger to smaller value of  $v$ , and simultaneously from lower to higher temperatures. The maximum density of water, on our model, is shifted by increase of pressure towards decreasing temperature, while at the same time it becomes less marked and finally vanishes; also in agreement with experiment. <sup>1)</sup>

<sup>1)</sup> AMAGAT. Recherches sur les gaz.

v. D. WAALS. Arch. Néerl. Vol. XII. p. 457.

GRASSI. Ann. d. chim. 3. 31, p. 437. 1851.

**Chemistry.** — “*On ocimene*”. By Prof. P. VAN ROMBURGH. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of February 27, 1904).

At the December meeting 1900, I had the honour to submit to the Academy a communication on the essential oil from an *Ocimum Basilicum* L. which contains besides a large quantity of eugenol, a hydrocarbon of the formula  $C_{10}H_{16}$  to which I gave the name of *Ocimene*. The peculiar behaviour of that hydrocarbon reminded me of the olefinic terpenes, discovered by SEMMLER, of which myrcene, isolated by POWER and KLEBER, was the best known. *Ocimene*, however, did not appear to be identical with myrcene.

CHAPMAN<sup>1)</sup> has shown some time ago that the essential oil of hops contains 40—50 % of an olefinic terpene which he considers to be identical with myrcene. In his paper, CHAPMAN disagrees with my observation that myrcene is not so changeable as stated by POWER and KLEBER. According to these investigators this substance becomes polymerised after standing for a week, whereas I could preserve it for months, of course in a properly sealed bottle. CHAPMAN refers to a paper of HARRIES<sup>2)</sup> to show the unstability of myrcene. There we read, however, only that the polymerisation “sehr leicht zu bewirken ist durch längeres Stehen oder durch mehrstündiges Erhitzen auf 300°”, whilst SEMMLER<sup>3)</sup>, in accordance with my observations, says that he found it to be “überhaupt nicht so leicht veränderlich”.

The olefine terpene from hops has the power of absorbing oxygen, like *ocimene*. In one of CHAPMAN's experiments 16 cc. of oxygen were absorbed in three days by 1 cc. of the terpene. I had already found previously that myrcene does not absorb in the same time any notable quantity (only fractions of a cc.) and, recently, on repeating my experiments I found my previous observation confirmed. If, however, myrcene was left in contact with oxygen for a long time (in tubes 1.5 cm. in diameter) the volume of the gas began to decrease gradually, but with increasing velocity, so that after 16 days 30 cc. had been absorbed. Of a sample of *ocimene* which had been kept in a properly sealed bottle for three years and had twice made the journey to and from Java, 1 cc. absorbed 17.8 cc. of oxygen in 11 hours; in the case of this terpene I again noticed that after

<sup>1)</sup> Journ. of the Chem. Soc. Trans 1903. 83 p. 505.

<sup>2)</sup> Berl. Ber. 35 (1902). S. 3259.

<sup>3)</sup> Berl. Ber. 34 (1901). S. 3126.

oxidation had set in, the absorption proceeded more rapidly so that on the second day, for instance, oxygen was being absorbed at the rate of 2 cc. *per hour*.

Still, I should not feel justified in saying that hops-terpene and myrcene are not identical, merely on account of the difference in oxygen absorption, because further experiments have taught me that under certain undefined conditions even this hydrocarbon may sometimes be left in contact with oxygen for a day without absorbing a notable quantity<sup>1)</sup>. But as soon as the absorption has commenced it proceeds at a fairly rapid rate.

By the action of oxygen a colorless viscous substance is obtained. I hope to refer to these experiments more fully later on.

In the same paper CHAPMAN expresses some doubts as to the "chemical individuality" of ocimene. Although I have already pointed out in my previous communication that the boiling point at 20 mm., the behaviour on distilling at the ordinary atmospheric pressure and the index of refraction of ocimene and myrcene differ considerably, I will now adduce additional facts which undoubtedly prove that ocimene and myrcene are different compounds.

Mr. C. J. ENKLAAR, who has taken up the study of ocimene in the Utrecht laboratory, repeated in the first place the determination of the index of refraction of this hydrocarbon and for a product carefully fractionated over metallic sodium he found  $n_D = 1.4872$  and  $n_D = 1.4867$ , which values satisfactorily agree with 1.4861 previously found by myself by means of another apparatus. For myrcene, POWER and KLEBER have found  $n_D = 1.4674$  whilst I had, previously, found 1.4685.

SEMLER (loc. cit.) has shown that myrcene is reduced by sodium and alcohol to dihydro-myrcene. On applying this reaction to ocimene, Mr. ENKLAAR obtained a dihydro-ocimene, which not only differs from dihydro-myrcene<sup>2)</sup> as regards boiling point, specific gravity and index of refraction, but also by the fact that it yields with bromine a *crystallised* additive compound. These investigations are being continued.

1) Not improbably, traces of moisture or of products of oxidation exercise a catalytic influence. A retardation was noticed when ocimene freshly distilled over metallic sodium was placed in dry oxygen.

2) Dihydro-ocimene boils at 168° at 763 mm. At 21 mm. the boiling point is 65°. Sp. gr. at 15° 0.775. The boiling point of dihydro-myrcene is 171°.5—173°.5 at the ordinary pressure and its sp. gr. 0.7802,

**Chemistry.** — “*Additive compounds of s. trinitrobenzene.*” By Prof. P. VAN ROMBURGH. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of February 27, 1904.)

A communication from JACKSON and CLARKE <sup>1)</sup> on additive compounds of substituted nitrobenzenes and dimethylaniline and another from HIBBERT and SUDBOROUGH <sup>2)</sup> on additive compounds of s. trinitrobenzene and alkylated arylamines induces me to call attention to the fact that I have been engaged for a long time with the study of the additive compounds of m. dinitro- and s. trinitrobenzene. In addition to those which I have described in former papers <sup>3)</sup> I have prepared a large number of compounds with different aromatic amines (such as toluidines, phenylendiamines, benzidine and their alkyl derivatives) which will be fully described elsewhere as soon as the crystallographic investigation of many of these products, kindly undertaken by Dr. F. M. JAEGER, has been concluded.

Besides with benzene and naphthalene <sup>4)</sup>, s. trinitrobenzene combines, like picric acid, with different aromatic hydrocarbons. It forms with *anthracene* fine orange-red needles (m.p. 161°), with a *methylanthracene* reddish colored needles (m.p. 138°), with *phenanthrene* an orange-yellow compound (m.p. 163°) <sup>5)</sup> with *fluorene* a yellow compound.

In all these compounds we find that 1 mol. of s. trinitrobenzene is combined with one mol. of the hydrocarbon.

s. Trinitrobenzene forms with  $\alpha$ -bromonaphthalene a fine lemon-yellow compound (m.p. 139°) and a similar one with dibenzylideneacetone.

Substituted aromatic amino-compounds such as anthranilic acid, and its methylester, p. aminoacetophenone, ethyl m. and p. aminobenzoate brought together with s. trinitrobenzene in alcoholic solution readily form colored well-crystallised compounds, the first two of which are colored orange and the others red. p. Aminobenzoic acid combines less readily and I have not succeeded in obtaining an additive compound with m. aminobenzoic acid, which is a stronger acid than its isomers.

Among the above compounds are some which will, presumably, prove of importance in the hands of the micro-chemist for the detection of certain substances.

<sup>1)</sup> Berl. Ber. **37**, (1904), S. 177.

<sup>2)</sup> Journ. Chem. Soc. **83** p. 1334.

<sup>3)</sup> Rec. d. Trav. chim. d. Pays-Bas **6**, 366; **7**, 3, 228; **8**, 274; **14**, 65.

<sup>4)</sup> HEPP, Ann. d. Chemie **215**, S. 376.

<sup>5)</sup> In the Dutch publication of this article, the melting point has been stated incorrectly.

**Botany.** — “*Determination of the action of poisons on plants.*” By Prof. E. VERSCHAFFELT. (Communicated by Profs. C. A. LOBRY DE BRUYN and HUGO DE VRIES.)

When a part of a living organ of a land-plant is placed in water it usually absorbs water on account of the well-known osmotic properties of the protoplasm and this absorption goes on until the cell-walls allow of no further extension. The accompanying increase in volume and the phenomena of tension in the tissue which may result therefrom, have, since HUGO DE VRIES laid the foundations of the subject, given rise to many an investigation which it will be superfluous to mention here again. Evidently this absorption of water will also cause the weight of the fragment of tissue to increase and it is easily understood that fairly considerable differences in weight will arise as soon as the organ is somewhat rich in parenchym.

All this only happens however as long as the part of the plant is alive. When a part of an organ that has been previously killed is placed in water, no more water is absorbed; on the contrary, since the semipermeability of the protoplasm has been destroyed, the dissolved substances of the cell-sap diffuse out; with them part of the water that stretches the cell-wall leaves the fragment of tissue, and this latter diminishes in weight as well as in volume.

Hence it seems possible, by determining the changes in weight, subsequent upon placing a plant-organ in water, to decide whether this latter is alive or dead. If it turns out that no other circumstances have a disturbing influence, we should have a new criterion for determining the lethal limit of measurable external circumstances, besides the diffusion of colouring matter at the death of plant-cells<sup>1)</sup>, used by HUGO DE VRIES, and the non-appearance of the plasmolytic phenomenon, recently applied by A. J. J. VAN DE VELDE<sup>2)</sup>. In order to test the practicableness of the method I tried to determine in this way the toxic limit of a few substances and it seems to me that this has been successful. Not every arbitrarily chosen plant-organ can be expected to lend itself equally well for these experiments; most of them proved serviceable, however, and as very fit for this purpose I mention the potato-tuber, beetroot, fleshy leaves of *Aloe*, juicy leaf-stalks like those of *Begonia*, *Rheum* and other plants.

One example may illustrate the proceeding and give an idea about the observed differences in weight.

<sup>1)</sup> Arch. Néerl. VI, 1871.

<sup>2)</sup> Transactions of the four first Flemish Physical and Medical Congresses (Dutch).

After a preliminary experiment had proved that the toxic limit of  $\text{Cu SO}_4$  for potato lay below a concentration of 0,005 grammol. per litre, four fragments of potato were dried with filtering-paper, weighed, and placed in solutions of  $\text{Cu SO}_4$  containing:

*a* 0,001; *b* 0,002; *c* 0,003 and *d* 0,004 gr. mol.

The bits of potato weighed respectively:

*a* 3,775; *b* 3,225; *c* 2,860 and *d* 3,195 gr.;

After having stayed in the solutions for 24 hours, they were dried and weighed again, the results being:

*a* 4,620; *b* 3,310; *c* 2,895 and *d* 3,260 gr.

So they all had absorbed water; the toxic effect of the cupric sulphate penetrating at the same time would now soon become apparent, however. The bits were washed and placed in water from the supply (water from the dunes); after 24 hours they weighed:

*a.* 4,670; *b.* 3,350; *c.* 2,825 and *d.* 3,150 gr.

This time *c.* and *d.* had lost weight and this loss increased steadily during the following day, whereas *a* and *b* went on absorbing water. The toxic limit of  $\text{Cu SO}_4$  for bits of potato weighing 3—5 grammes consequently lies, after 24 hours, between 0,002 and 0,003 grammol. per litre, i.e. between 0,03 and 0,05 per cent (molecular weight of  $\text{Cu SO}_4 = 159$ ).

Henceforth a piece of tissue was considered undamaged if, after having stayed in the poisonous solution for 24 hours and then for another 48 hours in water (once or twice renewed), it had, at all events, not lost weight, if it had not gained. It is obvious that in these experiments only such organs can be used as will remain alive for a fairly long time, when immersed in water. I can state concerning potatoes, that normal fragments, placed in water which was daily renewed, even after 18—20 days did not lose weight but absorbed small quantities of water. It made no difference, at least within this period of time, whether water from the supply or distilled water was used. In all similar experiments the results obtained by weighing are confirmed in a striking manner by the circumstance that bits of potato, when they die off, turn dark-grey (conversion of tyrosine into homogentisinic acid by enzyme-action). Also various other parts of plants show some similar phenomenon which may serve as a check, in the first place the diffusion of colouring matter, as with red beetroot, *Begonia* and others.

In the manner described above, also the harmful limit of concentration may be determined of neutral mineral salts which in a certain dilution are innocuous for a long time, but in more concen-

trated solutions must necessarily become harmful if it were only on account of their strong osmotic action on plant-cells; in other words, it is possible to determine the toxic limit of plasmolysing substances. In these cases the results of weighing are different in that the tissues in the salt-solution obviously lose weight but recover weight again when placed in water, if they have remained undamaged. If during the *deplasmolysis* death might occur, this can afterwards be recognised by a diminution of weight.

By this method I have been able to ascertain that the potato-tuber is rather sensitive for plasmolysing agents. Pieces of this organ appear to be damaged when they have stayed for 24 hours in 0.4 grammol. NaCl (2.34%), and are then placed in water. We will not decide whether death took place already in the salt-solution or on entering the water; sometimes, however, the grey discoloration already began to appear in the solution. A solution of 0.3 grammol. NaCl (1.75%) is perfectly harmless when acting for a day. Now other parts of plants offer a much greater resistance to neutral salts. The limiting concentration of NaCl for pieces of beetroot, e.g., lies, when acting for a day, at between 1 and 1.5 grammol.; I did not determine this limit more accurately. Similar values are furnished by various other parts of plants, such as the tuber of *Colchicum autumnale*; the leaf of *Aloe dichotoma* and *Aloe succotrina*.

For KBr, KNO<sub>3</sub>, the molecular concentration at which pieces of potato begin to be injured is pretty much the same as that given above for NaCl. For the present, however, it was not my intention to extend this investigation to a greater number of salts, although this would undoubtedly lead to many interesting results, also perhaps concerning the action of ions on the living cell. It only must be mentioned here that with glucose and saccharose, injurious effects on pieces of potato began to be noticeable at a concentration of 0.5 or 0.6 grammol. which is only slightly higher than with NaCl.

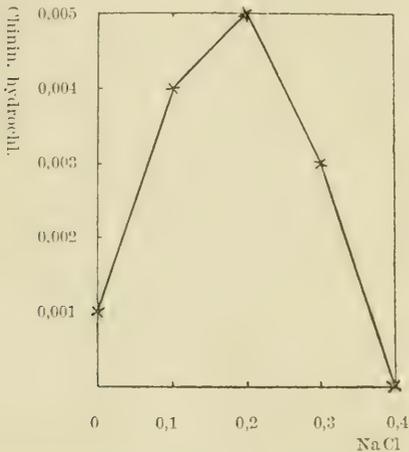
Interesting observations on the action of salt-solutions on plant-cells have been formerly made by J. C. COSTERUS<sup>1)</sup>; although they have not been repeated by the weighing-method, I must not omit drawing attention to them, since they seem to point to a different behaviour of the cells in the salt-solution, depending on the presence or absence of oxygen, which may be of importance with regard to what follows.

The determination of the lowest limit of concentration for which substances are poisonous, led us to investigate whether this limit can

<sup>1)</sup> Arch. Néerland. t. 15. 1880.

be shifted by adding other compounds to the solution. This is indeed often the case, and so the weighing-method lends itself to a repetition of the experiments of KAHLENBERG and TRUE<sup>1)</sup> and those of TRUE and GIES<sup>2)</sup> in which by a different method the toxicity of metallic compounds was proved to be diminished by the addition of certain salts. The case which I have examined a little more closely does not concern a metallic poison, however, but an alkaloid.

The lowest poisonous concentration of chinine hydrochloride for potato is a very low one, namely 0.001 grammol. per litre<sup>3)</sup>, the action lasting 24 hours. All parts of plants which I examined, proved to be about equally sensitive to this poison. The result of adding NaCl in a certain concentration to the chinine solution, is that after the same time, death occurs at a considerably higher concentration



of the chinine, this concentration depending again on the amount of NaCl in the solution. The figure represents graphically this shifting of the toxic limit. One sees from it that by 0.2 grammol. NaCl per litre the harmful concentration of the chinine hydrochloride is raised from 0.001 to 0.005 grammol., a further addition of salt acting less favourably again. At 0.4 grammol., as was pointed out before, pure NaCl is injurious to the potato.

As far as I have been able to gather, the toxic action of chinine hydrochloride on plants generally is modified in the same sense by NaCl. At any rate I obtained the same results with pieces of sugar-beetroot, the leaf-stalk of *Begonia*, fragments of the leaves of *Aloe*. As the cells of the sugar-beetroot resist much higher concentrations of common salt than those of the potato, it is not surprising that also in the presence of more than 1 grammol. NaCl per liter the antagonistic action towards chinine can be observed with this plant.

The diminution of toxicity, observed by the above-mentioned authors when certain salts, harmless in themselves, are added to metallic compounds, has been ascribed in most cases to the concentration of toxic ions being decreased; their results agree with the connection

1) Botan. Gazette. vol. 22, 1896.

2) Bulletin Torrey Botan. Club. vol. 30, 1903.

3) or 0,03965 ‰; mol. weight of  $C_{20}H_{24}N_2O_2 \cdot HCl + 2H_2O = 396,5$ .

between disinfecting power and degree of dissociation<sup>1</sup>), formerly studied by PAUL and KRÖNIG. Antitoxic actions of metal on metal with animal cells as reagent, studied by LOEB, proved however that the explanation cannot always be sought in this direction<sup>2</sup>). So a deeper interpretation of the case here mentioned must be put off for the present, the more as, very likely, it will appear not to belong to the domain of physiology but of chemistry.

The observations may be completed with the results of some experiments with other compounds.

The toxicity of chinine hydrochloride for potato and for sugar-beetroot is as clearly as by NaCl diminished by KBr, Li Br,  $\text{Ca}(\text{NO}_3)_2$ , which are rather different salts. Glucose and saccharose, on the other hand, have no influence whatever.

Also of another organic poison, namely oxalic acid, the action proved to be partially neutralised by NaCl being also present in the solution. Especially the sugar-beetroot gave very distinct results here, although also with the potato the antitoxic influence of the salt was clear. In a less degree, but yet in an unmistakable manner, the toxicity of oxalic acid is counteracted by saccharose.

Some experiments with a metallic poison (cupric salts) gave results which were in general concordant with those of KAHLENBERG and his collaborators.

### Physiology. — *“On some applications of the string galvanometer”.*

By Prof. W. EINTHOVEN. Communication from the Physiological laboratory at Leyden.

In a former paper<sup>3</sup>) the amount of sensitiveness of the string galvanometer and the time in which the deflections of the quartz-thread are accomplished were mentioned and illustrated by a few photograms. We stated that with a feeble tension of the wire a current of  $10^{-12}$  Amp. could still be observed and that with a stronger tension, so that the movement of the wire is still dead-beat and the sensitiveness is reduced to a deflection of 1 mm. for  $2 \times 10^{-8}$  Amp., a deflection of 20 mm. requires about 0.009 seconds.

<sup>1</sup>) Zeitschr. für physikal. Chemie. Bd. 12. 1896. Zeitschr. für Hygiene. Bd. 25. 1897.

<sup>2</sup>) PFLÜGER'S Archiv. Bd. 88. 1901. Americ. Journ. of physiol. vol. 6. 1902

Other observations belonging to the same category of animal physiology, were recently made by E. LESNÉ and CH. RICHTER FILS, (Arch. internat. de Pharmacodynamie. XII. 1903).

<sup>3</sup>) These Proc. June 27. 1903. p. 107.

These data may be sufficient to form an opinion about the instrument in theory and to give an idea of its fitness for practical work; yet on this latter point the applications alone can give full and convincing evidence.

In what follows we intend to mention some of these applications.

Where the object is to measure very feeble currents no other galvanometer seems to equal the instrument we are considering. It is obvious that theoretically there is no limit to the sensitiveness of any arbitrary galvanometer for constant currents. One can indefinitely increase the period of oscillation of the magnets as well as the distance of the scale and so obtain any desired sensitiveness in theory. But practical difficulties soon draw a limit. One among other difficulties is the inconstancy of the zero-point, which is influenced by many circumstances and which causes the more trouble the more the period of oscillation increases.

This is probably the reason why an electrometer is preferred to a galvanometer when very feeble currents have to be measured, e. g. when great insulating resistances have to be examined or the ionising power of radio-active substances.

In the celebrated investigation by Mr. and Mrs. CURIE<sup>1)</sup>, which led to the discovery of radium, the radio-activity of various materials was judged by their power to render air conductive; and the conductivity of the air was measured by means of an electrometer. The electrometer had to be charged by a current, which passed through a conducting layer of air, the rate at which the electrometer was charged being a measure for the current.

Evidently it was not an easy matter to measure currents in this way; so Mr. and Mrs. CURIE preferred a method of compensation by means of a rod of piezo-electric quartz. The charge received by the electrometer through the layer of conductive air was compensated by a contrary charge derived from the quartz-rod. To effect this the rod was subjected to a steadily increasing pull by continuously adding weight to a scale suspended on the quartz-rod. In this way the image of the mirror of the electrometer had to be kept at zero, the increase of the pull during the time being the measure for the current and in this case also for the conductivity of the air.

It is much easier to make these measurements with the string galvanometer.

I connected the instrument with two brass plates  $A_1$  and  $A_2$ , fig. 1.

<sup>1)</sup> See e.g. Mme SKŁODOWSKA CURIE, Recherches sur les substances radioactives, Annales de Chimie et de Physique 7, T. 30, p. 99. 1903.

Both plates were round, had a diameter of about 25 cm., were insulated and mounted at a distance of about 2 cm. from each other; the laboratory-battery of about 60 Volts and a resistance of 1 Megohm were inserted in the circuit from the galvanometer  $G$  to the plates.

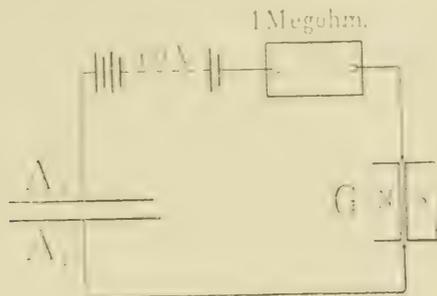


Fig. 1.

The sensitiveness of the galvanometer was adjusted at 1 mm. deflection for  $2 \times 10^{-11}$  Amp., the time required for a deflection being about 5 to 7 seconds. Now a round plate, covered over a diameter of about 20 cm. with powdered uranium-trioxide (containing water) was shoved in between  $A_1$  and  $A_2$  and laid on  $A_1$ . The galvanometer now showed a deflection of 2.5 mm. As soon as the uranium-preparation was removed it pointed exactly zero again.

The uranium-preparation was in this way repeatedly brought between the plates of the condenser and taken away again and each time the galvanometer showed the same deflection of exactly 2.5 mm. Each measurement was made in from 5 to 7 seconds; since, as has been shown before, a deviation of 0.1 mm. can still be noticed, the probable error of the observations may be put at  $\frac{1}{4}$  per cent.

The current measured amounted to  $5 \times 10^{-11}$  Amp., a value of the same order as that calculated by Mrs. CURIE for other uranium-compounds which had been examined under similar circumstances by means of the piezo-electrometer.

We will briefly mention some experiments with a few milligrams of a radium-salt. When the radium was placed between the condenser plates, a P. D. of 2 Volts proved sufficient to deflect the image of the wire a few centimetres. With a P. D. of 40 Volts in the circuit the same effect could be obtained by holding the radium-preparation at a distance of 1 metre from the plates. A definite distance of the radium from the plates corresponded to a definite indication of the galvanometer and it was obviously easy to drive the image from the scale by approaching the radium. It was remarkable in all these experiments that when the preparation of uranium or radium was

not moved, the deflection of the galvanometer also remained steady.

These observations also show how easy it is to measure an insulating resistance with the string galvanometer. The experiment with the uranium-trioxide showed that the resistance of the layer of air between the two plates of the condenser amounted to  $\frac{60 \text{ Volts}}{5 \times 10^{-11} \text{ Amp.}} = 1.2 \times 10^{12}$  Ohms or rather more than a million Megohms. An insulating resistance of  $6 \times 10^{13}$  Ohms can be demonstrated with the 60 Volts laboratory-battery by a lasting deflection.

We finally mention another application of the string galvanometer for measuring very feeble currents, namely those which are caused by atmospheric electricity. A spirit-lamp is held up on a long pole in the open air. An insulated wire connects the flame with one terminal of the galvanometer-wire, the other terminal being earthed. Under these conditions one sees a lasting deviation of the galvanometer which diminishes and disappears as soon as the pole is lowered and carried indoors, but which returns as soon as it is taken out and held up again.

The deflection of the galvanometer in these experiments was generally more or less oscillating on account of the wind causing fluctuations in the contact of the flame and the end of the wire.

Besides for measuring feeble currents, the wire-galvanometer is suitable in practical work for detecting small quantities of electricity and especially for accurately measuring rapid variations of electric tension or of feeble electric current. As the instrument for feeble currents which is quickest in its indications, it will undoubtedly prove useful for transoceanic telegraphy.

The smallest quantity of electricity that can be detected by it, can easily be calculated. Let us imagine that a great resistance has been inserted in the circuit so that the electromagnetic damping of the moving wire may be neglected and that now suddenly a current of constant intensity is sent through the wire.

The movement of the wire under these circumstances is accurately represented in the formerly published photograms <sup>1)</sup>. Theoretically the wire will, at the moment the current starts, experience an electromagnetic force by which an acceleration will be imparted to it. Its motion will be an accelerated one until a speed is attained such that the resultant of the electromagnetic force and the tension of the wire will make equilibrium with the resistance of the air.

<sup>1)</sup> These Proc. June 27, 1903. p. 107.

If however the tension of the wire is feeble enough, the duration of this accelerated motion is very small compared with the total duration of the deflection so that it may be neglected. We are then allowed to speak of an initial velocity of the wire and may disregard its mass. The initial velocity is proportional to the current and may be estimated at about 20 mm. per second for a current of  $10^{-9}$  Amp. with an image as is obtained with our magnification <sup>1)</sup>).

A current then of  $10^{-9}$  Amp. only needs to last for  $\frac{1}{200}$  sec. to cause a deviation of 0.1 mm. and as the photograms prove such a deviation to be still visible, a quantity of electricity of  $5 \times 10^{-12}$  Ampère-seconds can consequently be detected. This quantity is equal to the charge of a condenser of 1 microfarad at a potential of  $5 \times 10^{-6}$  Volts or to the charge of a sphere of 4.5 cm. radius at a potential of 1 Volt.

Since, as was pointed out above, the initial velocity is proportional to the current, the deflection for a small quantity of electricity, will entirely depend on that quantity itself, and it will make no difference whether a strong current passes during a short time or a feeble current during a longer time, if only the time of passage be small enough.

The properties of the wire-galvanometer lead us to expect another very remarkable consequence. If the tension of the wire is increased, the velocity with which a deflection is accomplished, will increase, but at the same time the amount of the deflection for a given current will diminish. Now it has already appeared from the photograms that, *provided the tension of the wire is not too great*, the change in sensitiveness is exactly inversely proportional to the change in deflectional velocity, so that the initial velocity for a given current is independent of the tension of the wire. From this we derive the seemingly paradoxical result that under the condition mentioned the deviation for a quickly passed, small quantity of electricity is the same for any tension of the wire.

The facts are in complete accordance with this argument and for an observer who is not accustomed to the instrument, it is very curious to see, how with a relatively much greater tension of the wire and a consequent great diminution in sensitiveness for constant

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<sup>1)</sup> This amount of 20 mm. is only approximately true. I hope soon to be able to deal more extensively with the movement of the wire under various conditions. The influence of the viscosity of the air will then be compared with that of the electromagnetic damping. It would be a decided advantage if the wire could be placed in an air-tight space, which would enable us to observe its deflections either in a vacuum or under increased pressure.

currents, the sensitiveness for a quickly passed small quantity of electricity remains nearly unaltered.

And the practical application lies at hand. Whenever rapid variations in electric tension have to be discovered and the disturbance by slowly varying currents has to be avoided, a requirement which frequently imposes itself in electro-physiological investigations, the wire must be relatively strongly stretched.

The described sensitiveness for small and quickly passing quantities of electricity, more even than its sensitiveness for constant currents, makes the wire-galvanometer a suitable research-instrument for a number of phenomena which are usually observed by means of an electrometer.

If one end of the wire is earthed, the other joined to an insulated conductor, e.g. a resistance-box, a rubbed ebonite rod, brought near the resistance-box, will act by influence and easily drive the image from the scale. A single advancing or receding movement of the rod must obviously result in a double movement of the wire, since this latter always returns to zero when the rod stops moving. At a distance of a few metres, rubbing the rod with a silk cloth will still cause deviations of the galvanometer, each single stroke of the hand occasioning a to and fro movement of the wire.

When I had laid aside the ebonite rod and the silk cloth and came near the resistance-box with the hand only, a small deflection of a few millimetres could still be observed. When quickly approaching the hand, the wire showed a momentary deviation in one direction, when quickly withdrawing it, in the opposite sense. Even moving the fingers round one of the plugs of the resistance-box caused the wire to move. It must be emphasised that the resistance-box was not touched by the hand so that ordinary conduction from the body through the galvanometer to the earth was out of the question.

I could not at once explain the phenomenon. My first thought was that the body or at any rate the hand was charged to a certain potential and like the ebonite rod drove electricity by influence through the resistance-box and the galvanometer. But the potential of one of the hands of an uninsulated person is too small to explain the movement of the wire.

Also clothing, e.g. a woollen sleeve, appeared to play no part. If a round metal disk connected to the earth by a conducting wire and hence having presumably the same potential as the galvanometer and the resistance-box, was suddenly brought near or removed from

the latter, the same deviations were noticed as when moving the human hand.

Also these deflections changed only little when the metal disk was moved, after having been charged by a storage-cell to a potential of  $+ 2$  or  $- 2$ .

The idea that the strange phenomenon had to be ascribed to currents in the air which would generate electricity by friction, had to be rejected at once, as soon as, by means of a pair of bellows, a powerful air-current had been directed against the resistance-box without the wire showing the least motion. But in the end the explanation appeared to be very simple. The ebonite plate of the resistance-box has a certain charge and the lines of electric force bend from the ebonite to the metal plugs. As soon as a conductor now approaches, the lines of force are displaced and thus electricity is moved from the metal through the galvanometer to the earth.

That this is the real explanation could be easily shown by rubbing the ebonite of the resistance-box and so charging it to a higher potential. When this was done the deviations became many times larger.

An interesting proof of the usefulness of the wire-galvanometer as a sensitive instrument which at the same time is quick in its indications, is afforded by the ease and accuracy with which it registers sounds.

When a SIEMENS' telephone is connected with the galvanometer, the sound-vibrations falling on the plate of the telephone will send induced currents through the wire, by which this latter will be moved.

As soon as a tone of arbitrary pitch is made to sound against the telephone with constant intensity, the image of the wire broadens in a curious way. In the bright field the narrow, black image is broadened to a band of several centimetres breadth, which has a light grey tint and whose appearance in the field is feebler as it is broader. The middle of the grey band always corresponds to the image of the quartz-thread in rest. The margins have a somewhat darker delineation than the rest of the band.

This appearance is entirely explained by the circumstance that the wire executes regular, rapid vibrations of the same rhythm as the sound-vibrations striking the telephone.

One peculiarity has still to be mentioned. If a sound like *a* or *o* is sung against the telephone-plate, one sees the grey band divided into parts. Symmetrically with respect to the middle of the image, within its real margins something like secondary and tertiary margins

are visible which admit of no other explanation than that the motion of the wire, representing the sound in its fundamental and partial tones, consists of a number of vibrations of different frequencies and amplitudes.

We hope soon to analyse this phenomenon photographically. When the intensity of the sound is changed, the breadth of the grey band also changes immediately. And at the moment the sound stops, one sees the narrow, black image of the wire standing perfectly still again in the bright field.

When the telephone is replaced by a microphone and a suitable induction-coil, the same phenomena are observed; with these contrivances however the arrangement has become much more sensitive. Feeble sounds now give rise to considerable broadening and it is surprising to see, how, when one speaks softly at a distance of one or more metres from the microphone, the image of the wire reacts powerfully on each word that is spoken or rather on each syllable that is pronounced, but always immediately occupies its position of rest as soon as the sound stops for a moment.

Feeble sounds, as e.g. the cardiac sounds of a rabbit are excellently rendered by the galvanometer.

Besides for the study of phonetics and of cardiac sounds, the wire-galvanometer will find fruitful applications over an extensive range of physiological research. We already communicated some results of an investigation concerning the human electrocardiogram <sup>1)</sup>. Besides, an investigation of the nerve-currents is now in course of progress, about which we will only mention in this place that the action-currents of a nerve, resulting upon simple stimulation, can be shown and registered in an excellent manner. As far as I know action-currents of the ischiadic of a frog, arising by the stimulus at the make and break of an ascending and of a descending constant current, have never been observed hitherto. The string galvanometer shows them in all their details as they must be expected according to PFLÜGER's law of contractions and the existence of which could until now only be surmised from the observed muscular contractions. One also sees the superposition of the phenomena of electrotonus on those of the action-current, which need be no impediment to the interpretation of the obtained curves. We seem to be justified in supposing that perhaps new points of view will be opened about the manner in which the nerve is capable of reacting on various stimuli.

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<sup>1)</sup> l. c.

**Chemistry.** — “*Action of hydrogen peroxyde on diketones 1,2 and on  $\alpha$ -ketonic acids.* By Prof. A. F. HOLLEMAN.

Some aromatic acids may be obtained by first introducing the acetyl group by means of the reaction of FRIEDEL and CRAFTS and oxidising this to the carboxyl group. In many cases, however, this oxidation does not take place readily; the group  $\text{CO} \cdot \text{CH}_3$  yields with comparative ease the group  $\text{CO} \cdot \text{CO}_2\text{H}$  but the further transformation of the latter into the carboxyl group is often attended with great loss. Even the method of HOOGEWERFF and VAN DORP, consisting in heating the  $\alpha$ -ketonic acid with concentrated sulphuric acid does not yield the theoretical quantity. I have tried whether this transformation might perhaps be attained quantitatively by means of hydrogen peroxide, according to the equation:



This was indeed the case. Aqueous solutions of pyruvic acid, benzoylformic acid, thiénylglyoxylic acid when heated with the calculated amount of 30 % hydrogen peroxyde (MERCK) at once eliminated CO and yielded almost quantitative amounts of acetic acid, benzoic acid and thiophenic acid. From Prof. EYKMAN, I received small specimens of four  $\alpha$ -ketonic acids which he is investigating and these, when heated in aqueous or acetic acid solution with a slight excess of  $\text{H}_2\text{O}_2$  also eliminated CO. On titrating the acids obtained from them it was found that their group  $\text{CO} \cdot \text{CO}_2\text{H}$  had passed into  $\text{CO}_2\text{H}$ .

This result led us to suppose that  $\alpha$ -diketones might also be readily resolved by the action of  $\text{H}_2\text{O}_2$ ,



Some of the diketones, such as benzil, camphorquinone and phenanthrenequinone were dissolved in glacial acetic acid and warmed for some days with a small excess of 30 %  $\text{H}_2\text{O}_2$ . The expected reaction took place almost quantitatively: it was remarkable that camphorquinone did not at once yield camphoric acid but first the anhydride, which was converted by boiling with dilute alkali into camphoric acid.

Messrs. J. HUISINGA and J. W. BEEKMAN have carried out the experiments.

Groningen, March 1904.

Lab. Univers.

**Mathematics.** — “On a decomposition of a continuous motion about a fixed point  $O$  of  $S_3$  into two continuous motions about  $O$  of  $S_3$ 's” by Mr. L. E. J. BROUWER, communicated by Prof. KORTEWEG.

(Communicated in the meeting of February 27, 1904).

Two planes in  $S_3$  making two equal angles of position are called mutually “equiangular to the right” if one is (with its normal plane) plane of rotation for an equiangular double rotation to the right about the other one and its normal plane.

We will call the sides of one and the same acute angle of position “corresponding vectors” through the point of intersection of two equiangular intersecting planes.

As is known a system of planes equiangular to the right or to the left is infinite of order two. Of course a determined equiangular system of planes to the right can have with a determined equiangular system of planes to the left not more than one pair of planes in common (two pairs of planes cannot intersect each other at the same time equiangularly to the right and to the left); but *one* pair of planes they always have in common. We will show how that common pair of planes can be found.

A pair of intersecting pairs of planes of both systems is of course easy to find. We lay through any vector  $OC$  the planes belonging to the two systems; their normal planes intersect each other in a second vector  $OD$ . Thus  $OCD$  is one plane of position of those two pairs of planes. In the second plane of position the four planes furnish four lines of intersection, let us say  $OH$ ,  $OF$ ,  $OK$ ,  $OG$ , in such a way, that the considered pairs of planes must be  $OCH$ ;  $ODK$  and  $OCF$ ;  $ODG$ . The following figures are supposed to be situated in those two planes of position.

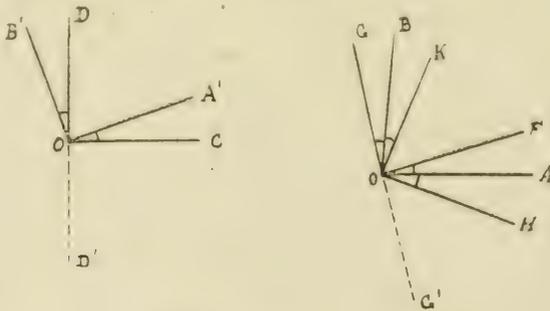


Fig. 1.

Let the pair of planes  $OCH$ ;  $ODK$  belong to the given system equiangular to the right, and  $OCF$ ;  $ODG$  to the given system equiangular to the left.

The vectors in the second plane of position are drawn in such a way that either

$$\begin{cases} OH \rightarrow OC \\ OK \rightarrow OD \end{cases} \dots \dots \dots (1)$$

is an equiangular double rotation to the right, or that such is the case with

$$\begin{cases} OH \rightarrow OC \\ OK \rightarrow OD' \end{cases}$$

We shall suppose the first to be true (the reasoning is the same for the second case). Then

$$\begin{cases} OF \rightarrow OC \\ OG \rightarrow OD \end{cases}$$

is also an equiangular double rotation to the right: for, the planes  $OFC$  and  $OGD$  can be brought to coincide with these directions of rotation with the planes  $OHC$  and  $OKD$ , having the directions of rotation

$$\begin{cases} OH \rightarrow OC \\ OK \rightarrow OD \end{cases}$$

So

$$\begin{cases} OF \rightarrow OC \\ OG \rightarrow OD \end{cases} \dots \dots \dots (2)$$

is an equiangular double rotation to the left.

If furthermore  $OA$  and  $OB$  are bisectors of the angles  $HOF$  and  $KOG$ , and if we have made  $\angle COA' = \angle DOB' = \angle HOA = = \angle FOA = \angle KOB = \angle GOB$ , then the pair of planes

$$\begin{cases} AOA' \\ BOB' \end{cases}$$

is a pair of planes of rotation as well for the equiangular double rotation to the right (1) as for the equiangular double rotation to the left (2). So it is the pair of common planes which was looked for of the two systems of planes.

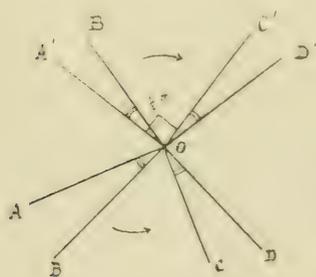


Fig. 2.

drawn upwards lie in  $\delta$  and those drawn downwards in  $\gamma$ .

We shall think now that through two arbitrary vectors  $OA$  and  $OB$  two planes intersecting each other equiangularly to the left have been laid: we shall now consider more closely the position which two such planes have with respect to the plane  $OAB$  and its normal plane. We shall call the indicated equiangular planes to the left  $\alpha$  and  $\beta$ ; and indicate  $OAB$  by  $\gamma$  and its normal plane by  $\delta$ . In fig. 2 the lines

The plane  $OCC'$  is the plane of position of  $\gamma$  and  $\alpha$ , intersected by  $\gamma$  in  $OF$ , by  $\alpha$  in  $OC$ . Fig. 3 is supposed to lie in that plane of position. We have made fartheron in fig. 1 the angles  $A'OB'$ ,  $C'OD'$ ,  $COD$  equal to  $\angle AOB = \varphi$ , and the directions of rotation indicated in those planes belong to a double rotation to the right. Fig. 4 is supposed to lie in the plane  $ODD'$ , and the lines  $OG$  and  $OG'$  are drawn in it in such a way, that  $ODGD'G' \cong OCFC'F'$ .

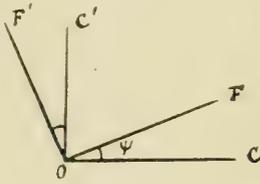


Fig. 3.

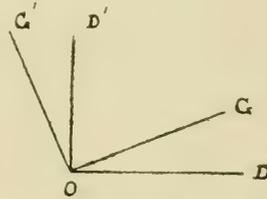


Fig. 4.

We shall consider the plane  $BOG$  more closely. Let us project  $OB$  and  $OG$  both on  $\alpha$ , then it is not difficult to see that the execution of those two operations, each of which is threedimensional, gives as a result two lines  $OH$  and  $OK$ , mutually perpendicular (see fig. 5, supposed to lie in  $\alpha$ ).

The projecting planes are successively:  $OBF'$  (fig. 6) and  $OGA'$  (fig. 7).

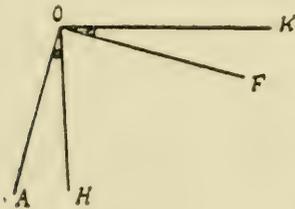


Fig. 5.

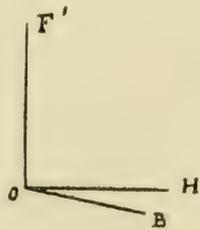


Fig. 6.

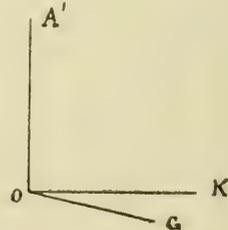


Fig. 7

We shall directly see that  $OB$  and  $OF'$  are situated on different sides of  $OH$ , and  $OG$  and  $OA'$  on different sides of  $OK$ , and that  $\angle HOB = \angle KOG$ , if we suppose ourselves to be successively in the threedimensional spaces, in which the projecting takes place.

So we see that the plane  $BOG$  has two mutually perpendicular vectors, making equal angles with  $\alpha$  and projecting itself on  $\alpha$  according to two perpendicular vectors namely  $OB$  and  $OG$ , projecting themselves according to  $OH$  and  $OK$ : the characteristic of equiangular intersection.

Let us still examine of which kind that equiangular intersection is; we shall then perceive that on account of  $OB$  being transferred into  $OG$  by the equiangular double rotation

$$OF' \rightarrow OA'$$

$$OH \rightarrow OK$$

and this being of the same kind as

$$OF' \rightarrow OA'$$

$$OA \rightarrow OF$$

which in its turn can be made to coincide with

$$OC' \rightarrow OA'$$

$$OA \rightarrow OC$$

by a single rotation about the plane  $OAA'$ , the kind of equiangular intersection is the same as the kind of the double rotation

$$OC' \rightarrow OA'$$

$$OA \rightarrow OC$$

which is to the left according to the data.

So the plane  $OBG$  is identical with the plane  $\beta$ , for through  $OB$  only *one* plane equiangular to the left with  $\alpha$  can pass.

If we now introduce the notation “ $\begin{pmatrix} ab \\ cd \end{pmatrix}$  equiangular to the right” indicating if  $abcd$  denote four vectors through  $O$ , that the planes  $(ab)$  and  $(cd)$  are equiangular to the right and that the same double equiangular rotation to the right transferring  $a$  into  $b$ , also transfers  $c$  into  $d$ , then

$$\begin{pmatrix} OA, OB \\ OF, OG \end{pmatrix}$$

is equiangular to the right and the corresponding equiangular double rotation to the right transfers  $\alpha$  into  $\beta$ . In other words we have proved the

Theorem 1. If  $\begin{pmatrix} ab \\ cd \end{pmatrix}$  is equiangular to the right, then  $\begin{pmatrix} ac \\ bd \end{pmatrix}$  is equiangular to the left; or in other words though less significant:

By an equiangular double rotation to the right any plane passes into one equiangular to it to the left.

If we suppose three vectors  $abc$  (whose position of course determines the position of  $S_4$ ) to have come after some equiangular double rotations to the right into the position  $dcf$ , then  $\begin{pmatrix} ab \\ de \end{pmatrix}$  is equiangular to the left and  $\begin{pmatrix} ac \\ df \end{pmatrix}$  equiangular to the left: so  $\begin{pmatrix} ad \\ be \end{pmatrix}$  equiangular to the right and  $\begin{pmatrix} ad \\ cf \end{pmatrix}$  equiangular to the right, so finally

$$\begin{pmatrix} ad \\ be \\ cf \end{pmatrix}$$

equiangular to the right: in other words the final position would have been obtainable out of the initial position by a single equiangular double rotation to the right; with which is proved:

*Theorem 2.* Equiangular double rotations of the same kind form a group.

Let us suppose given two equiangular systems to the right and two vectors  $OA$  and  $OB$  through each of which we bring the planes belonging to both systems; then the equiangular double rotation to the left, transferring  $OA$  into  $OB$ , will transfer at the same time the angle of position formed in  $OA$  into the one formed in  $OB$ , thus:

*Theorem 3.* Two equiangular systems to the right form in each vector the same angle, which can be called the angle of the two systems.

The obtained results we shall verify by deducing analytically theorems 1 and 3, which deduction will also throw some more light.

Suppose a rectangular system of coordinates to be given in such a way that

$$\begin{pmatrix} OX_2, OX_3 \\ OX_1, OX_4 \end{pmatrix}$$

is equiangular to the right. The same then holds good for

$$\begin{pmatrix} OX_3, OX_1 \\ OX_2, OX_4 \end{pmatrix} \text{ and } \begin{pmatrix} OX_1, OX_2 \\ OX_3, OX_4 \end{pmatrix}.$$

A vector  $a$  through  $O$  we can determine by its four cosines of direction  $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ .

A plane passing through the vectors  $a$  and  $\beta$  with direction of rotation from  $a$  to  $\beta$ , is determined by its six coefficients of position (i. e. projections of a vector unity)  $\lambda_{23}, \lambda_{31}, \lambda_{12}, \lambda_{14}, \lambda_{24}, \lambda_{34}$ , which are defined by the following relations, if we represent  $\alpha_2\beta_3 - \alpha_3\beta_2$  by  $\xi_{23}$ :

$$\lambda_{23} = \frac{\xi_{23}}{+ \sqrt{\xi_{23}^2 + \xi_{31}^2 + \xi_{12}^2 + \xi_{14}^2 + \xi_{24}^2 + \xi_{34}^2}}, \text{ etc.}$$

We must take the positive sign in the denominator, for  $\lambda_{23}$  must be positive, when the projection of  $a$  on  $OX_2OX_3$  to that of  $\beta$  on  $OX_2OX_3$  rotates through an angle less than  $\pi$  in the same way as  $OX_2$  to  $OX_3$ ; and in that same case  $\xi_{23}$  gives us a positive value. If we now represent that positive root of the denominator by  $K$ , then

$$\lambda_{23} = \frac{\xi_{23}}{K}; \lambda_{31} = \frac{\xi_{31}}{K}, \text{ etc.}$$

An equiangular double rotation to the right can be given by the

system of equiangular planes of rotation to the right with direction and the angle of rotation.

For all those planes of rotation

$$\lambda_{23} + \lambda_{14}$$

$$\lambda_{31} + \lambda_{24}$$

$$\lambda_{12} + \lambda_{34}$$

have the same values. These three values  $a_1, a_2, a_3$ , besides the cosinus of the angle of rotation  $a_4$ , we can take as determining quantities of the equiangular double rotation to the right. A rotation  $< 2\pi$  is unequivocally determined by that (for, whether the angle of rotation is  $\begin{matrix} > \\ < \end{matrix} \pi$ , which is left undecided by the value of the cosinus, follows from the sign of the  $a_1, a_2, a_3$ ).

Suppose an arbitrary vector  $a$  to be transferred by the rotation into  $\beta$ , then it holds good for each pair of vectors  $a\beta$  that:

$$a_2 \beta_3 - a_3 \beta_2 + a_1 \beta_4 - a_4 \beta_1 = K \cdot a_1$$

$$a_3 \beta_1 - a_1 \beta_3 + a_2 \beta_4 - a_4 \beta_2 = K \cdot a_2$$

$$a_1 \beta_2 - a_2 \beta_1 + a_3 \beta_4 - a_4 \beta_3 = K \cdot a_3$$

$$a_1 \beta_1 + a_2 \beta_2 + a_3 \beta_3 + a_4 \beta_4 = a_4$$

If however we consider that  $K = +\sqrt{\sin^2 \vartheta}$ , if  $\vartheta$  is the angle of rotation, then  $K$  proves to be a constant for all pairs of vectors so that we may regard  $K \cdot a_1, K \cdot a_2, K \cdot a_3$  and  $a_4$  as determining quantities of the double rotation which we shall call  $\pi_1, \pi_2, \pi_3, \pi_4$ ; and we shall write the relations:

$$\left. \begin{aligned} -a_1 \beta_1 - a_3 \beta_2 + a_2 \beta_3 + a_4 \beta_4 &= \pi_1 \\ a_3 \beta_1 - a_1 \beta_2 - a_1 \beta_3 + a_2 \beta_4 &= \pi_2 \\ -a_2 \beta_1 + a_1 \beta_2 - a_4 \beta_3 + a_3 \beta_4 &= \pi_3 \\ a_1 \beta_1 + a_2 \beta_2 + a_3 \beta_3 + a_4 \beta_4 &= \pi_4 \end{aligned} \right\} \dots \dots (H)$$

in which we have at the same time arranged the first members according to  $\beta_1, \beta_2, \beta_3, \beta_4$ . We now perceive:

$$\begin{aligned} \pi_1^2 + \pi_2^2 + \pi_3^2 + \pi_4^2 &= K^2 \{ (\lambda_{23}^2 + \lambda_{31}^2 + \lambda_{12}^2 + \lambda_{11}^2 + \lambda_{24}^2 + \lambda_{34}^2) + \\ &\quad + 2(\lambda_{23}\lambda_{14} + \lambda_{31}\lambda_{24} + \lambda_{12}\lambda_{34}) \} + a_4^2 \\ &= K^2 (1 + 2 \times 0) + a_4^2 \\ &= \sin^2 \vartheta + \cos^2 \vartheta \\ &= 1. \end{aligned}$$

So we can regard  $\pi_1, \pi_2, \pi_3, \pi_4$  as cosines of direction of a vector through  $O$  in  $S_4$  and we can represent an equiangular double rotation to the right by a vector through  $O$  in  $S_4$ , which determines it

unequivocally. (A vector *without* length; later on we shall determine it, likewise unequivocally, by a vector *with* length, in  $S_3$ ).

If we furthermore consider the determinant on the coefficients of  $\beta_1, \beta_2, \beta_3, \beta_4$  in (H) it proves to satisfy all the conditions of an orthogonal transformation.

We call that transformation with that determinant

$$\begin{array}{cccc} -\alpha_4 & -\alpha_3 & +\alpha_2 & +\alpha_1 \\ +\alpha_3 & -\alpha_4 & -\alpha_1 & +\alpha_2 \\ -\alpha_2 & +\alpha_1 & -\alpha_4 & +\alpha_3 \\ +\alpha_1 & +\alpha_2 & +\alpha_3 & +\alpha_4 \end{array}$$

the  $(+r)$   $\alpha$ -transformation; it appears in the relations (H), if the first members are arranged according to the cosines of direction of the final position of the rotating vector. If they are arranged according to the cosines of direction of the initial position the determinant of the coefficients becomes

$$\begin{array}{cccc} \beta_4 & \beta_3 & -\beta_2 & -\beta_1 \\ -\beta_3 & \beta_4 & \beta_1 & -\beta_2 \\ \beta_2 & -\beta_1 & \beta_4 & -\beta_3 \\ \beta_1 & \beta_2 & \beta_3 & \beta_4, \end{array}$$

which we shall call the  $(-r)$   $\beta$ -transformation.

Quite analogous to this we have for equiangular double rotations to the left ( $\varrho_1 \varrho_2 \varrho_3 \varrho_4$ ) bilinear homogeneous equations between the cosines of direction of initial and final position of a vector, let us say  $\alpha$  and  $\beta$ , which arranged according to the  $\beta$ 's, give as determinant of the coefficients

$$\begin{array}{cccc} \alpha_4 & -\alpha_3 & \alpha_2 & -\alpha_1 \\ \alpha_3 & \alpha_4 & -\alpha_1 & -\alpha_2 \\ -\alpha_2 & \alpha_1 & \alpha_4 & -\alpha_3 \\ \alpha_1 & \alpha_2 & \alpha_3 & \alpha_4, \end{array}$$

the  $(+l)$   $\alpha$ -transformation and arranged according to the  $\alpha$ 's

$$\begin{array}{cccc} -\beta_4 & \beta_3 & -\beta_2 & \beta_1 \\ -\beta_3 & -\beta_4 & \beta_1 & \beta_2 \\ \beta_2 & -\beta_1 & -\beta_4 & \beta_3 \\ \beta_1 & \beta_2 & \beta_3 & \beta_4, \end{array}$$

the  $(-l)$   $\beta$ -transformation.

We can now state the following:

If the equiangular double rotation to the right ( $\alpha_1 \alpha_2 \alpha_3 \alpha_4$ ) transfers the vector  $(\alpha_1 \alpha_2 \alpha_3 \alpha_4)$  into  $(\beta_1 \beta_2 \beta_3 \beta_4)$  then the  $(+r)$   $\alpha$ -transformation transfers the vector  $(\alpha_1 \alpha_1 \alpha_3 \alpha_4)$  into  $(\beta_1 \beta_2 \beta_3 \beta_4)$

and the  $(-i)$   $\beta$ -transformation transfers the vector  $(\pi_1, \pi_2, \pi_3, \pi_4)$  into  $(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$ .

Analogous to this:

If the equiangular double rotation to the left  $(\varrho_1, \varrho_2, \varrho_3, \varrho_4)$  transfers the vector  $(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$  into  $(\beta_1, \beta_2, \beta_3, \beta_4)$ , then the  $(+l)$   $\alpha$ -transformation transfers the vector  $(\varrho_1, \varrho_2, \varrho_3, \varrho_4)$  into  $(\beta_1, \beta_2, \beta_3, \beta_4)$

and the  $(-l)$   $\beta$ -transformation transfers the vector  $(\varrho_1, \varrho_2, \varrho_3, \varrho_4)$  into  $(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$ .

Let us now suppose that  $S_4$  has first an equiangular double rotation to the right  $(\pi)$  transferring an arbitrary vector  $\alpha$  into  $\beta'$ ; then an equiangular double rotation to the left  $(\varrho)$ , transferring  $\beta'$  into  $\gamma$ , then we can write:

$$\begin{aligned} \pi &= [(+r) \alpha] \beta' & \varrho &= [(-l) \gamma] \beta' \\ \pi &= \{[(+r) \alpha] \cdot [(-l) \gamma]\} \varrho \end{aligned}$$

where the form between  $\{\}$  denotes the determinant of transformation having as first row the sum of the products of the terms of the first row of  $[(+r) \alpha]$  with the corresponding ones of respectively the first, second, third and fourth of  $[(-l) \gamma]$ , whilst the second etc. row in a corresponding manner is deduced out of the second etc. row of  $[(+r) \alpha]$  (all this in the way of forming a product of determinants).

If  $S_4$  has first an equiangular double rotation to the left  $(\varrho)$  transferring  $\alpha$  into  $\beta''$  and then an equiangular double rotation to the right  $(\pi')$ , transferring  $\beta''$  into  $\gamma$ , we have:

$$\begin{aligned} \varrho &= [(+l) \alpha] \beta'' & \pi' &= [(-r) \gamma] \beta'' \\ \pi' &= \{[(-r) \gamma] \cdot [(+l) \alpha]\} \varrho. \end{aligned}$$

But now

$$[(+r) \alpha] \cdot [(-l) \gamma] \equiv [(-r) \gamma] \cdot [(+l) \alpha]$$

which can be at once verified, so:

$$\pi' \equiv \pi.$$

Thus:

If  $S_4$  is allowed successively an equiangular double rotation to the right  $(\pi)$  and one to the left  $(\varrho)$  the order of the two rotations may be interchanged. For, in both cases an initial position of a vector  $\alpha$  gives the same final position  $\gamma$ .

And if we regard the quadruple  $\alpha, \beta', \beta'', \gamma$ , then  $\begin{pmatrix} \alpha & \beta' \\ \beta'' & \gamma \end{pmatrix}$  is equiangular to the right, according to the rotation  $(\pi)$  and  $\begin{pmatrix} \alpha & \beta'' \\ \beta' & \gamma \end{pmatrix}$  equiangular to the left according to the rotation  $(\varrho)$ ; by which we assuredly once more have proved theorem 1.

Let us furthermore suppose  $(\sigma)$  and  $(\tau)$  to be two equiangular double rotations to the right, transferring a given vector  $\varepsilon$  the former into  $\zeta$ , the latter into  $\eta$ . Then

$$\sigma = [(+ r) \varepsilon] \zeta \quad \tau = [(+ r) \varepsilon] \eta.$$

The same orthogonal transformation transferring  $\sigma$  into  $\zeta$ , transfers  $\tau$  into  $\eta$ , so that the angle between  $\zeta$  and  $\eta$  is the angle between the vectors  $\sigma$  and  $\tau$  independent of the initial position  $\varepsilon$ . As a special case theorem 3 is included in this, for the case that the two double rotations take place about an angle  $\frac{1}{2} \pi$ ; for then the angle between  $\zeta$  and  $\eta$  is the angle of the two planes of rotation through  $\varepsilon$ , proving to be independent of  $\varepsilon$ .

We have still to mention that theorem 1 in the second form is entirely included in the applications of the biquaternions on  $S_4$  as given by Dr. W. A. WITTHOFF in his dissertation: "De Biquaternion als bewerking in de ruimte van vier afmetingen" (the biquaternion as an operation in fourdimensional space). For an equiangular double rotation to the right is represented by  $Q \cdot \varepsilon_1 + \varepsilon_2$  (p. 127) where  $Q$  represents a certain quaternion with norm unity.

This applied to an arbitrary double vector

$$a_1 \varepsilon_1 + a_2 \varepsilon_2,$$

changes it into

$$Q a_1 \varepsilon_1 + a_2 \varepsilon_2,$$

so it leaves the isosceles part of that double vector to the left unchanged and so also the equiangular system of planes to the left to which it belongs. This holds good for an arbitrary double vector, so particularly for a plane.

Finally theorem 3 can be proved as follows:

If  $\varphi$  and  $\psi$  are the acute angles of position of two planes, then if we represent the coefficients of position respectively by  $\lambda$ 's and  $\mu$ 's:

$$\begin{aligned} \cos \varphi \cos \psi &= \lambda_{23} \mu_{23} + \lambda_{31} \mu_{31} + \lambda_{12} \mu_{12} + \lambda_{14} \mu_{14} + \lambda_{24} \mu_{24} + \lambda_{34} \mu_{34} = \\ &= \Sigma (\lambda_{23} + \lambda_{14}) (\mu_{23} + \mu_{14}) - \Sigma (\lambda_{23} \mu_{14} + \lambda_{14} \mu_{23}). \end{aligned}$$

For intersecting planes with angle of position  $\varphi$ :

$$\cos \varphi = \Sigma (\lambda_{23} + \lambda_{14}) (\mu_{23} + \mu_{14}) = \Sigma (\lambda_{23} - \lambda_{14}) (\mu_{23} - \mu_{14}).$$

So for two intersecting planes, belonging to two definite equiangular systems to the right or two to the left

$$\lambda'_{23} + \lambda'_{14} = \lambda''_{23} + \lambda''_{14} \quad \text{and} \quad \mu'_{23} + \mu'_{14} = \mu''_{23} + \mu''_{14}$$

resp.  $\lambda'_{23} - \lambda'_{14} = \lambda''_{23} - \lambda''_{14}$  and  $\mu'_{23} - \mu'_{14} = \mu''_{23} - \mu''_{14}$  and  $\cos \varphi' = \cos \varphi''$ .

We shall now resume our geometrical reasoning dropped after theorem 3. Let us take through  $O$  a definite vector  $OW$  in  $S_4$  but not movable with  $S_4$  and let us represent each system of planes equi-

angular to the right by the line of intersection of the plane through  $OW$  belonging to it with  $S_3 \perp OW$ . That  $S_3$  is thus, entirely filled with these representing lines which are in (1,1)-correspondence with the represented systems of planes.

We shall call that  $S_3 \perp OW$  regarded as a complex of the rays representing the equiangular to the right systems of planes, "the representing  $S_3$  to the right of  $S_4$ " or shorter "the  $S_r$  of  $S_4$ ". In the same way we form the " $S_l$  of  $S_4$ ". Each pair of planes in  $S_4$  is then unequivocally determined by its representants in  $S_r$  and  $S_l$  and reversely the pair of planes determines unequivocally its representants.

*Theorem 4.* An equiangular double rotation to the right of the  $S_4$  about a certain equiangular system to the right which double rotation leaves according to theorem 1 the position of  $S_l$  unchanged, gives a rotation of  $S_r$  about the representant of the system of the planes of rotation over an angle equal to double the angle, over which the equiangular double rotation to the right of  $S_4$  takes place.

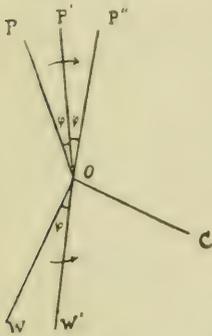


Fig. 8.

Let  $OP$  be an arbitrary vector in  $\beta$  and  $\varphi$  the angle, over which the equiangular double rotation to the right takes place. The double rotation leaves  $OC$  unchanged as representant of the equiangular system to the right on  $(\alpha\beta)$ . Moreover it transfers  $OW$  into  $OW'$  and  $OP$  into  $OP'$ . If we then still make  $\angle P''OP'$  equal to  $\angle P'OP$  we have :

$(OP, OP')$   
 $(OW, OW')$  equiangular to the right, thus :

$(OP', OP)$   
 $(OW, OW')$  equiangular to the left, or also :

$(OP'', OP')$   
 $(OW, OW')$  equiangular to the left, so at last

$(OP'', OW)$   
 $(OP', OW')$  equiangular to the right.

The plane  $POW$  giving  $OP$  as representant of its equiangular system to the right before its double rotation, gives after that rotation (transferred to  $P'OW'$ ) as representant  $OP''$  making an angle  $2\varphi$  with  $OP$ ; so an arbitrary vector  $OP$  in  $S_r \perp OC$  (the invariable vector) rotates about  $OC$  over an angle  $2\varphi$ , with which the theorem is proved.

We can now say: For an  $S_4$  moving as a solid about a fixed point the position is at every moment determined by its "position to the right" (the position of the  $S_r$  moving as a solid about a fixed point) and its "position to the left" (the position of  $S_l$ ). For, if of two positions the pairs of planes through  $O$  coincide, then this is the case too for all planes, thus for all rays too.

N.B. We can remark by the way, that in this way we have proved quite synthetically that two positions of  $S_4$  have a common pair of planes, namely that pair, which has as representants the axis of rotation of the two positions to the right and that of the two positions to the left; so, taking into consideration that also the common fixed point is always there (having as projections on the positions of planes remained invariable the centres of rotation of the projections of  $S_4$  on it), that the double rotation is the most general displacement of  $S_4$ . However, until now we have occupied ourselves only and wish to keep doing so with the motions of  $S_4$ , where always the same point  $O$  is in rest.

For a continuous motion of  $S_4$  the position and the condition of motion are at every moment determined by  $S_r$  and  $S_l$ ; so the motion of  $S_4$  is quite determined by the motions of  $S_r$  and  $S_l$ ; and at every moment the resulting displacement of  $S_4$  is quite determined by that of  $S_r$  and of  $S_l$ , independent of the order of succession or combining of the two latter; they have no influence upon each other. We can regard a motion of  $S_4$  as a sum of two entirely heterogeneous things, i. e. which cannot influence each other in any way or be transformed into each other.

We can proceed another step by indicating not only by a line in  $S_r$  a system of equiangular planes of rotation to the right, but also by a line vector along it an equiangular velocity of rotation to the right, that line vector being equal in size to the double velocity of rotation of the double rotation and directed along the vector moving with  $S_4$  in the direction of  $OW$ . Then equal and opposite velocities of rotations to the right of  $S_4$  are indicated by equal and opposite vectors in  $S_r$ .

Let  $OP_r$  be such an indicating vector and  $OQ_r$  and  $OS_r$  two mutually perpendicular vectors in the plane erected perpendicularly

to  $OP_r$  in  $S_r$  in such a way that

$$\begin{pmatrix} OP_r, OW \\ OQ_r, OS_r \end{pmatrix}$$

is equiangular to the right, then to the equiangular double rotation to the right of  $S_4$ , indicated by  $OP_r$ , corresponds the rotation of  $S_r$  about  $OP_r$  equal to the length of  $OP_r$  in the direction of  $OQ_r \rightarrow OS_r$ .

Let  $OP'_r$  be another indicating vector and let us determine in an analogous way  $OQ'_r$  and  $OS'_r$ , then the orthogonal systems of vectors

$$OWP_r Q_r S_r \text{ and}$$

$$OWP'_r Q'_r S'_r$$

are congruent, can thus be made to coincide by a rotation of  $S_4$ , with  $OW$ , thus  $S_r$  too, remaining in its place, so that the indicating vector  $OP_r$  by a motion of  $S_r$  in itself can be made to coincide with the indicating vector  $OP'_r$  in such a way, that at the same time the directions of rotation of  $S_r$  belonging to it coincide in the normal planes. But then an indicating vector in  $S_r$  represents that velocity of rotation entirely in the way usual in space of three dimensions, as also by its length it indicates the size of the velocity of rotation of  $S_r$  belonging to it; if namely we endeavour to regard the definition of that usual mode of representation entirely apart from the notion "motion with or against the hands" which is lacking in  $S_4$ ; and say simply after having taken in that space a system of coordinates  $OX_r Y_r Z_r$ : the vector of rotation will be erected to that side of the plane of rotation, that for the plane of rotation being by motion inside the space made to coincide with the plane of  $XY$  in such a way, that the direction of rotation runs from  $OX$  to  $OY$ , the vector of rotation is directed along the positive axis of  $Z$ .

For us that system of coordinates in  $S_r$ :  $OX_r, OY_r, OZ_r$  has been chosen in such a way that with  $OW$  it forms a system of coordinates in  $S_4$ , for which

$$\begin{pmatrix} OY_r, OZ_r \\ OX_r, OW \end{pmatrix}, \begin{pmatrix} OZ_r, OX_r \\ OY_r, OW \end{pmatrix}, \begin{pmatrix} OX_r, OY_r \\ OZ_r, OW \end{pmatrix}$$

are equiangular to the right.

A vector along  $OX_r$  then indicates a rotation of  $S_r$  in the sense of  $OY_r \rightarrow OZ_r$ .

Entirely analogous reasonings hold good for  $S_l$ . It being however more profitable to be able to say also for  $S_l$ : a vector along  $OX_l$  represents a velocity of rotation of  $S_l$  in the sense of  $OY_l \rightarrow OZ_l$ , we must modify the preceding either by choosing the system  $OX_l Y_l Z_l W$  in such a way that

$$\begin{pmatrix} OY_l, OZ_l \\ OX_l, OW \end{pmatrix}$$

is no more equiangular to the right, but to the left, or if we suppose

$$\begin{pmatrix} OY_l, OZ_l \\ OX_l, OW \end{pmatrix}$$

to be also equiangular to the right, we must take as indicating vector in  $S_l$  that vector in the direction of which  $OW$  would move together with  $S_4$ , not the one moving together with  $S_4$  in the direction of  $OW$ . We shall do the latter. The advantage of this choice will be evident from what follows.

We have still to remark, that if only the position of  $S_r$  and  $S_l$  is determined, the position of  $S_4$  ensues from it not in one, but in two ways; for, a position of  $S_4$  gives no other positions of  $S_r$  and  $S_l$  as its "opposite position" for which all vectors are reversed; that opposite position can be obtained by an arbitrary equiangular double rotation over an angle  $\pi$ ;  $S_r$  and  $S_l$  then rotate  $2\pi$  and are again in their former position.

But a continuous motion of  $S_4$  out of a given initial position is unequivocally determined by the given continuous movements of  $S_r$  and  $S_l$  out of the corresponding initial positions. So we shall have completely answered the question how a solid  $S_4$  moves under the action of determined forces if we can point out how  $S_r$  and  $S_l$  move under those actions; in other words if we can point out "the cones of rotation in the solid and in space".

#### APPLICATION. The Euler motion in $S_4$ .

The equations of motion for this have been given for the first time by FRAHM in the "Mathematische Annalen" Band 8, 1874 p. 35. The system of coordinates  $OX_1 X_2 X_3 X_4$  in the solid we shall choose in such a way that the products of inertia disappear. We shall suppose

$$\begin{pmatrix} OX_2, OX_3 \\ OX_1, OX_4 \end{pmatrix}$$

to be equiangular to the right.

And we choose  $OX_r Y_r Z_r$  and  $OX_l Y_l Z_l$  in such a way that:

$$\begin{pmatrix} OX_1, OX_2, OX_3, OX_4 \\ OX_r, OY_r, OZ_r, OW \end{pmatrix}$$

is equiangular to the right and

$$\begin{pmatrix} OX_1, OX_2, OX_3, OX_4 \\ OX_l, OY_l, OZ_l, OW \end{pmatrix}$$

equiangular to the left, (from which ensues as a matter of fact that also

$$\begin{pmatrix} OX_r, OY_r \\ OZ_r, OW \end{pmatrix} \text{ and } \begin{pmatrix} OX_l, OY_l \\ OZ_l, OW \end{pmatrix}$$

are equiangular to the right).

The systems  $OX_r Y_r Z_r$  and  $OX_l Y_l Z_l$  execute the motions of  $S_r$  and  $S_l$  which are to be considered.

Let us farther call  ${}_2\omega_3, {}_3\omega_1, {}_1\omega_2, {}_1\omega_4, {}_2\omega_4, {}_3\omega_4$  the components of the velocities of rotation according to the system  $OX_1 X_2 X_3 X_4$ ; and  $\varphi_1, \varphi_2, \varphi_3$  the components of the velocities of rotation of  $S_r$  according to  $OX_r, OY_r, OZ_r$ , likewise  $\psi_1, \psi_2, \psi_3$  the components of the velocities of rotation of  $S_l$  according to  $OX_l, OY_l, OZ_l$ . Then we know the components of velocity of rotation to the right

$$\frac{1}{2}({}_2\omega_3 + {}_1\omega_4) \text{ according to } \begin{matrix} OX_2 \rightarrow OX_3 \\ OX_1 \rightarrow OX_4 \end{matrix} \text{ or according to } \begin{matrix} OY_r \rightarrow OZ_r \\ OX_r \rightarrow OW \end{matrix}$$

and analogues, and likewise the components of velocity of rotation

$$\text{to the left } \frac{1}{2}({}_2\omega_3 - {}_1\omega_4) \text{ according to } \begin{matrix} OX_2 \rightarrow OX_3 \\ OX_4 \rightarrow OX_1 \end{matrix} \text{ or according to}$$

$$\begin{matrix} OY_l \rightarrow OZ_l \\ OW \rightarrow OX_l \end{matrix} \text{ and analogues.}$$

Therefore:

$$\begin{aligned} \varphi_1 &= {}_2\omega_3 + {}_1\omega_4 & \psi_1 &= {}_2\omega_3 - {}_1\omega_4 \\ \varphi_2 &= {}_3\omega_1 + {}_2\omega_4 & \psi_2 &= {}_3\omega_1 - {}_2\omega_4 \\ \varphi_3 &= {}_1\omega_2 + {}_3\omega_4 & \psi_3 &= {}_1\omega_2 - {}_3\omega_4 \end{aligned}$$

The Euler equations of motion "in the solid" (giving the opposite of the apparent motion of the surrounding space) follow more simply than according to FRAHM out of the vector formula

$$\text{fluxion of moment of motion} = \text{moment of force} - \text{rotation} \times \text{moment of motion}$$

which is easy to understand for a three dimensional space as well as for a four dimensional one,

(and where the sign  $\times$  indicates the vector product)

For, "in the space" the fluxion of the moment of motion = moment of force; but of this for the position in solid has already been marked the fluxion wanted to keep the position constant in the solid, i. e. the fluxion which corresponds to the rotation of the moment-vector about the rotationvector and this is = rotation  $\times$  moment of motion.

Let us call the squares of inertia  $\Sigma m x_1^2$  etc.  $P_1$  etc. and let us put

$$\begin{aligned}
 P_1 + P_2 + P_3 + P_4 &= R \\
 -P_1 + P_2 + P_3 - P_4 &= A_1 \\
 P_1 - P_2 + P_3 - P_4 &= A_2 \\
 P_1 + P_2 - P_3 - P_4 &= A_3.
 \end{aligned}$$

Then we can write the rotationvector in the form:

$${}_2\omega_3 i + {}_3\omega_1 j + {}_1\omega_2 k + h({}_1\omega_4 i + {}_2\omega_4 j + {}_3\omega_4 k)$$

or in the form

$$\varepsilon_1(\varphi_1 i + \varphi_2 j + \varphi_3 k) + \varepsilon_2(\psi_1 i + \psi_2 j + \psi_3 k).$$

The notations  $h$  and  $\varepsilon$  are taken from the above-named dissertation of Dr. W. A. WILTHOFF;  $h$  is defined on page 67;  $\varepsilon_1$  and  $\varepsilon_2$  on page 78.

The moment of motion becomes

$$\begin{aligned}
 (P_2 + P_3) {}_2\omega_2 i + (P_3 + P_1) {}_3\omega_1 j + (P_1 + P_2) {}_1\omega_2 k + \\
 + h\{(P_1 + P_4) {}_1\omega_4 i + (P_2 + P_4) {}_2\omega_4 j + (P_3 + P_4) {}_3\omega_4 k\}
 \end{aligned}$$

or in an other form

$$\begin{aligned}
 \frac{1}{2} \varepsilon_1 \{(R\varphi_1 + A_1 \psi_1) i + (R\varphi_2 + A_2 \psi_2) j + (R\varphi_3 + A_3 \psi_3) k\} + \\
 + \frac{1}{2} \varepsilon_2 \{(R\psi_1 + A_1 \varphi_1) i + (R\psi_2 + A_2 \varphi_2) j + (R\psi_3 + A_3 \varphi_3) k\}.
 \end{aligned}$$

If  $\varphi$  and  $\psi$  represent the rotation vectors in  $R_r$  and  $R_l$ , we can write the rotation:

$$\varepsilon_1 \varphi + \varepsilon_2 \psi,$$

and the moment

$$\frac{1}{2} R(\varepsilon_1 \varphi + \varepsilon_2 \psi) + (\frac{1}{2} \varepsilon_1 \cdot (A) \psi + \frac{1}{2} \varepsilon_2 \cdot (A) \varphi),$$

where the notation  $(A)\varphi$  means:  $A_1 \varphi_1 i + A_2 \varphi_2 j + A_3 \varphi_3 k$ .

The first and strongest of these terms falls along the rotationvector; for a body with equal squares of inertia it is the only one; the second, which, together with the  $A$ 's, becomes stronger as the body is more asymmetric, we might call the "crossed moment" because its right part is caused by the left part of the rotation and inversely.

Let us put finally the moment of force in the form  $\varepsilon_1 \mu + \varepsilon_2 \nu$ , where  $\mu$  and  $\nu$  are threedimensional vectors; then the above given formula of the vector can be broken up into the six following components, given successively by the coefficients of  $\varepsilon_1 i, \varepsilon_2 i, \varepsilon_1 j, \varepsilon_2 j, \varepsilon_1 k, \varepsilon_2 k$ .

$$\begin{aligned}
 R\dot{\varphi}_1 + A_1 \dot{\psi}_1 &= A_2 \psi_2 \varphi_3 - A_3 \psi_3 \varphi_2 + 2\mu_1 \\
 R\dot{\psi}_1 + A_1 \dot{\varphi}_1 &= A_2 \varphi_2 \psi_3 - A_3 \varphi_3 \psi_2 + 2\nu_1 \\
 R\dot{\varphi}_2 + A_2 \dot{\psi}_2 &= A_3 \psi_3 \varphi_1 - A_1 \psi_1 \varphi_3 + 2\mu_2 \\
 R\dot{\psi}_2 + A_2 \dot{\varphi}_2 &= A_3 \varphi_3 \psi_1 - A_1 \varphi_1 \psi_3 + 2\nu_2 \\
 R\dot{\varphi}_3 + A_3 \dot{\psi}_3 &= A_1 \psi_1 \varphi_2 - A_2 \psi_2 \varphi_1 + 2\mu_3 \\
 R\dot{\psi}_3 + A_3 \dot{\varphi}_3 &= A_1 \varphi_1 \psi_2 - A_2 \varphi_2 \psi_1 + 2\nu_3.
 \end{aligned}$$

If we put  $R^2 - A_p^2 = a_p$  and  $RA_p + A_q A_r = b_p$ , and if we represent the vector  $a_1 \varphi_1 i + a_2 \varphi_2 j + a_3 \varphi_3 k$ , by  $(a) \varphi$ , we can write the six equations of motion:

$$(a) \dot{\varphi} = V. (b) \psi . \varphi + 2Ru - 2Av$$

$$(a) \dot{\psi} = V. (b) \varphi . \psi + 2Rv - 2A\mu.$$

For absence of external forces:

$$\left. \begin{aligned} (a) \dot{\varphi} &= V. (b) \psi . \varphi \\ (a) \dot{\psi} &= V. (b) \varphi . \psi \end{aligned} \right\} \dots \dots \dots (h)$$

In this form we can directly read:

1<sup>st</sup>. If in the initial position  $\varphi = \psi$ , then  $\varphi$  remains equal to  $\psi$ , i. e. if the initial rotation of  $S_4$  is a rotation // to a principal space of inertia, then the motion remains a rotation // to that space. The equations of motion for that case can be reduced to a system to be treated as the well known Euler motion in  $S_3$  when the forces are missing.

2<sup>nd</sup>. For unequal  $A$ 's "invariable rotating" is only possible under the following two conditions which are éach in itself sufficient:

*a.* for  $\varphi$  and  $\psi$  both directed along one and the same axis of coordinate ( $X$ -,  $Y$ - or  $Z$ -axis of the representing spaces) i. e. for a double rotation of  $S_4$  about a pair of principal planes of inertia;

*b.* for  $\varphi = 0$  or  $\psi = 0$ , i. e. for an equiangular double rotation of  $S_4$ .

It has been pointed out by KÖTTER (see "Berliner Berichte" 1891, p. 47), how a system of equations analogous with what was given, can be integrated. (The problem treated there is the motion of a solid in a liquid). According to the method followed by him the six components of rotation can be expressed explicitly by hyper-elliptic functions in the time. If however we have  $\varphi_1, \varphi_2, \varphi_3, \psi_1, \psi_2, \psi_3$  expressed in the time, we have the "cones in the solid" for  $S_r$  and  $S_l$ . To deduce from these the "cones in space" we set about as follows. We notice that the moment of motion to the right  $R\varphi + (A) \psi$  in  $S_r$  remains invariable "in space" (in  $S_l$  that vector changes of course its direction, but there  $R\psi + (A) \rho$  remains invariable); calling the two spheric coordinates ("polar distance" and "length") of  $\varphi$  with respect to  $R\varphi + (A) \psi$  during the motion of  $\varphi$  in space  $\vartheta$  and  $\chi$  and remarking that each element of the "cone in space" at the moment of contact coincides with the corresponding element of the "cone in the solid", we can express  $\vartheta, \dot{\vartheta}$  and  $\dot{\chi}$  in the time, with which the

“cone in space” for  $S_r$  is found. Analogously the “cone in space” is determined for  $S_l$  with respect to  $R\psi + (A)\varphi$ .

We shall just show that as soon as two of the squares of inertia  $P$  become equal, which means the same as two  $A$ 's becoming equal we can do with usual elliptic functions only.

For instance let  $A_2 = A_3$ , thus also  $a_2 = a_3 = {}_2a_3$ ;  $b_2 = b_3 = {}_2b_3$ . Let us call  ${}_2\varphi_3$  and  ${}_2\psi_3$  the value of the decomponents of  $\varphi$  and  $\psi$  in the  $YZ$ -plane,  $r_\varphi$  and  $r_\psi$  the anomalies of those decomponents (counted from  $Y$  to  $Z$ ), and  $F$  the difference of anomaly of  ${}_2\psi_3$  and  ${}_2\varphi_3$ ; then the equations (h) become for this case:

$$\begin{aligned} a_1 \dot{\varphi}_1 &= - {}_2b_3 {}_2\varphi_3 {}_2\psi_3 \sin F & a_1 \dot{\psi}_1 &= {}_2b_3 {}_2\varphi_3 {}_2\psi_3 \sin F \\ {}_2a_3 \dot{\varphi}_3 &= {}_2b_3 \varphi_1 {}_2\psi_3 \sin F & {}_2a_3 \dot{\psi}_3 &= - {}_2b_3 {}_2\varphi_3 \psi_1 \sin F \\ \dot{r}_\varphi &= \frac{b_1}{{}_2a_3} \psi_1 - \frac{{}_2b_3}{{}_2a_3} \varphi_1 \cos F \frac{{}_2\psi_3}{{}_2\varphi_3} & \dot{r}_\psi &= \frac{b_1}{{}_2a_3} \varphi_1 - \frac{{}_2b_3}{{}_2a_3} \psi_1 \cos F \frac{{}_2\varphi_3}{{}_2\psi_3} \\ \dot{r} &= \frac{b_1}{{}_2a_3} (\varphi_1 - \psi_1) + \frac{{}_2b_3}{{}_2a_3} \cos F \left( \varphi_1 \frac{{}_2\psi_3}{{}_2\varphi_3} - \psi_1 \frac{{}_2\varphi_3}{{}_2\psi_3} \right) \end{aligned}$$

from which we deduce four integral relations between

$\varphi_1$ ,  ${}_2\varphi_3$ ,  $\psi_1$ ,  ${}_2\psi_3$  and  $F$ , namely

$$\varphi_1 + \psi_1 = \frac{c_1}{\sqrt{a_1}} \dots \dots \dots (I)$$

$${}_2a_3 {}_2\varphi_3^2 + a_1 \varphi_1^2 = c_2^2 \dots (II), \quad {}_2a_3 {}_2\psi_3^2 + a_1 \psi_1^2 = c_3^2 \dots (III)$$

$${}_2a_3 {}_2b_3 {}_2\varphi_3 {}_2\psi_3 \cos F + a_1 b_1 \varphi_1 \psi_1 = c_4 \dots \dots (IV)$$

If we put in these

$${}_2\varphi_3 = \frac{c_2}{\sqrt{{}_2a_3}} \cos \eta, \quad \varphi_1 = \frac{c_2}{\sqrt{a_1}} \sin \eta,$$

$${}_2\psi_3 = \frac{c_3}{\sqrt{{}_2a_3}} \cos \zeta, \quad \psi_1 = \frac{c_3}{\sqrt{a_1}} \sin \zeta,$$

we have the differential equations

$$\dot{\eta} = - \frac{{}_2b_3}{{}_2a_3 \sqrt{a_1}} c_3 \cos \zeta \sin F, \quad \dot{\zeta} = \frac{{}_2b_3}{{}_2a_3 \sqrt{a_1}} c_2 \cos \eta \sin F$$

with the two integrals:

$$c_2 \sin \eta + c_3 \sin \zeta = c_1,$$

$${}_2b_3 \cos \eta \cos \zeta \cos F + b_1 \sin \eta \sin \zeta = \frac{c_4}{c_2 c_3},$$

so that after elimination we obtain the following differential equation in  $\eta$ :

$$\begin{aligned} {}_2a_3^2 a_1 c_2^2 \cdot \cos^2 \eta \cdot \dot{\eta}^2 &= ({}_2b_3^2 - b_1^2) c_2^4 \sin^4 \eta \\ &\quad - 2 c_1 ({}_2b_3^2 - b_1^2) c_2^3 \sin^3 \eta \\ &\quad + \{ c_1^2 ({}_2b_3^2 - b_1^2) - (c_2^2 + c_3^2) {}_2b_3^2 - 2 c_4 \cdot b_1 \} c_2^2 \sin^2 \eta \\ &\quad + 2 c_1 (c_2^2 \cdot {}_2b_3^2 + c_4 \cdot b_1) c_2 \sin \eta \\ &\quad + c_2^2 (c_3^2 - c_1^2) {}_2b_3^2 - c_4^2 \end{aligned}$$

or  $c_2 \sin \eta (= \sqrt{a_1 \cdot \varphi_1})$  put equal to  $u$ :

${}_2a_3^2 a_1 u^2 = F_4(u)$ , in which we can easily verify that  $F_4(u)$  has two real roots between  $-c_2$  and  $+c_2$  (the two other roots are real outside those limits or imaginary according to  ${}_2b_3^2 - b_1^2$  being  $\begin{cases} > \\ < \end{cases}$  than 0); those two roots indicate the limits between which  $\eta$  swings to and fro according to a course indicated by elliptic functions. For the case  ${}_2b_3^2 > b_1^2$  for instance, thus for four real roots  $u_1 < u_2 < u_3 < u_4$ , that course becomes:

$$u = u_2 + \frac{{}_1u_2 \cdot {}_2u_3 \operatorname{sn}^2}{{}_1u_3 - {}_2u_3 \operatorname{sn}^2}, \text{ where } \operatorname{sn} \equiv \operatorname{sn} \left\{ \frac{1}{2} t \sqrt{\frac{{}_2u_4 \cdot {}_1u_2 ({}_2b_3^2 - b_1^2)}{{}_2a_3^2 a_1}} \right\},$$

and

$$p u_q \equiv u_q - u_p.$$

Farthermore:

$$F_{\varphi} = \frac{b_1}{{}_2a_3} \psi_1 - \frac{{}_2b_3}{{}_2a_3} \varphi_1 \frac{{}_2\varphi_3 \cdot {}_2\psi_3 \cos F}{{}_2\varphi_3^2}$$

where the second member is a rational function of  $\varphi_1$  ( $\psi_1$  can be rationally expressed in  $\varphi_1$  according to (I),  ${}_2\varphi_3^2$  according to (II),  ${}_2\varphi_3 {}_2\psi_3 \cos F$  according to (IV)), so that  $F_{\varphi}$  too can be expressed in  $t$  by elliptic functions and by that the entire “cone in the solid”; and further according to the above method also “the cone in space”.

The following special cases can very easily be traced to the end.

1<sup>st</sup>. The four squares of inertia are equal two by two. This case is obtained by putting  $A_2 = A_3 = 0$ .

Then

$$\begin{aligned} a_1 &= R^2 - A_1^2 & b_1 &= RA_1 \\ {}_2a_3 &= R^2 & {}_2b_3 &= 0. \end{aligned}$$

And the equations of motion pass into:

$$\begin{aligned} a_1 \dot{\varphi}_1 &= 0 & a_1 \dot{\psi}_1 &= 0 \\ {}_2a_3 {}_2\dot{\varphi}_3 &= 0 & {}_2a_3 {}_2\dot{\psi}_3 &= 0 \\ \dot{F}_{\varphi} &= \frac{b_1}{{}_2a_3} \psi_1 & \dot{F}_{\psi} &= \frac{b_1}{{}_2a_3} \varphi_1 \\ \dot{F} &= \frac{b_1}{{}_2a_3} (\varphi_1 - \psi_1) \end{aligned}$$

from which we directly read,  $\varphi_1$ ,  ${}_2\varphi_3$ ,  $\psi_1$  and  ${}_2\psi_3$  remaining constant, that the “cone in the solid” for  $S_r$  and for  $S_l$  is a cone of revolution with the  $X$  axis as axis of revolution. Farthermore the moment

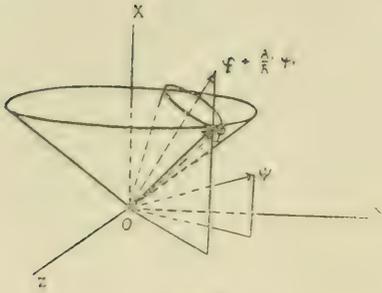


Fig. 9.

$R\varphi + A_1\psi_1$  to the right lying in the meridian plane of  $\varphi$  remains in  $S_r$  invariable. Thus “in space” that meridian plane rotates about the vector  $R\varphi + A_1\psi_1$ , by which the “cone in space” is known, and likewise proves to be a cone of revolution. Analogous for  $S_l$ . Fig. 9 shows the two cones of rotation in  $S_r$ . The outer cone is the moving one.

2<sup>nd</sup>. Three of the squares of inertia are equal and unequal to the fourth. We take the axis of the unequal one as  $X_4$  axis in  $S_4$ . Then  $A_1 = A_2 = A_3 = A$ ;  $a_1 = a_2 = a_3 = a$ ;  $b_1 = b_2 = b_3 = b$ ; and the equations (h) pass into

$$\dot{\varphi} = \frac{b}{a} V \psi \cdot \varphi$$

$$\dot{\psi} = \frac{b}{a} V \varphi \cdot \psi$$

therefore  $\dot{\varphi}$  and  $\dot{\psi}$  are both perpendicular to  $\varphi$  and to  $\psi$ , whilst  $\dot{\varphi} + \dot{\psi} = 0$ , so  $\varphi + \psi$  is constant and  $\varphi$  and  $\psi$  are each for itself constant in absolute value, so that they both rotate about their sum (“in space” that vector of the sum has in general quite a different position for  $S_r$  than for  $S_l$ ) by which the two “cones in the solid” are determined. “Invariable rotating” of  $S_4$  we have here wherever  $\varphi$  and  $\psi$ ,

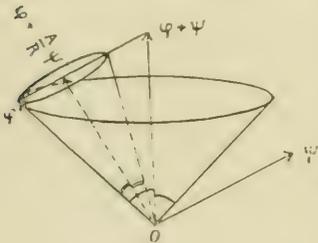


Fig. 10.

regardless of their value, coincide. To find the “cone in space” for  $S_r$ , we notice the invariability in  $S_r$  of  $R\varphi + A\psi$ . “In space”  $\varphi$  rotates about  $R\varphi + A\psi$ , for the angle between those two vectors remains constant. In  $S_l$  rotates analogously “in space”  $\psi$  about  $R\psi + A\varphi$ . Fig. 10 represents the two cones of rotations in  $S_r$ . (Here too the outer cone is the moving one).

We remind the readers once more, that where we bring  $\varphi$  and  $\psi$ , as far as their positions in the solid are concerned, into relationship with each other, we must of course in our mind make the positions to the right and the left that is of the systems of coordinates  $OX_r Y_r Z_r$  and  $OX_l Y_l Z_l$  to coincide with each other, so that but one system of coordinates  $OXYZ$  is left (for instance for the equations

(*h*) this must be noticed); but in space (i. e. the  $S_3 \perp OW$ ) those systems of coordinates  $OX_r Y_r Z_r$  and  $OX_l Y_l Z_l$  have at each moment very definite positions differing from one another.

**Chemistry.** — Prof. C. A. LOBRY DE BRUYN read also in the name of Mr. L. K. WOLFF a paper entitled: “*Can the presence of the molecules in solutions be proved by application of the optical method of TYNDALL?*”

(This paper will not be published in these Proceedings).

**Chemistry.** — Prof. C. A. LOBRY DE BRUYN presents also in the name of Prof. A. F. HOLLEMAN a paper by Dr. J. J. BLANKSMA, entitled: “*On the substitution of the core of Benzene.*”

(This paper will not be published in the Proceedings).



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday April 23, 1904.

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CONTENTS.

ERG. DRUOIS: "Facts leading to trace out the motion and the origin of the underground water in our sea-provinces." (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 738.

L. H. SIERTSEMA: "Investigation of a source of errors in measurements of magnetic rotations of the plane of polarisation in absorbing solutions." (Communicated by Prof. H. KAMERLINGH ONNES), p. 760.

FRED. SCHUIJ: "An equation of reality for real and imaginary plane curves with higher singularities." (Communicated by Prof. D. J. KORTEWEG and P. H. SCHOUTE), p. 764.

C. A. LOBRY DE BRUYN and C. H. SLUITER: "The BECKMANN-rearrangement: transformation of acetophenoxime into acetanilide and its velocity", p. 773.

C. L. JUNGUIS: "The mutual transformation of the two stereoisomeric pentacetates of *d*-glucose." (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 779.

P. H. SCHOUTE: "Regular projections of regular polytopes", p. 783.

L. E. J. BROUWER: "On symmetric transformation of  $S_4$  in connection with  $S_r$  and  $S_l$ ". (Communicated by Prof. D. J. KORTEWEG), p. 785.

PH. KOHNSTAMM: "On the equations of CLAUSIUS and VAN DER WAALS for the mean length of path and the number of collisions." (Communicated by Prof. J. D. VAN DER WAALS), p. 787.

PH. KOHNSTAMM: "On VAN DER WAALS' equation of state." (Communicated by Prof. J. D. VAN DER WAALS), p. 794.

J. REUDLER: Note on SYDNEY YOUNG'S law of distillation." (Communicated by Prof. J. D. VAN DER WAALS), p. 807.

H. A. LORENTZ: "Electromagnetic phenomena in a system moving with any velocity smaller than that of light", p. 809.

E. JAHNKE: "Observation on the paper communicated on Febr. 27 1904 by Mr. BROUWER: "On a decomposition of the continuous motion about a point  $O$  of  $S_4$  into two continuous motions about  $O$  of  $S_3$ 's." (Communicated by Prof. D. J. KORTEWEG), p. 831.

L. E. J. BROUWER: "Algebraic deduction of the decomposability of the continuous motion about a fixed point of  $S_4$  into those of two  $S_3$ 's." (Communicated by Prof. D. J. KORTEWEG), p. 832.

A. A. W. HUBRECHT: "On the relationship of various invertebrate-phyla", p. 839.

MAX. WEBER: "On some of the results of the Siboga-expedition", p. 846.

L. BOLK: "The dispersion of the blonde and brunette type in our country", p. 846.

R. P. VAN CALCAR and C. A. LOBRY DE BRUYN: "Changes of concentration in and crystallisation from solutions by centrifugal power", p. 846.

C. L. JUNGUIS: "Theoretical consideration concerning boundary reactions, which decline in two or more successive phases." (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 846.

The following papers were read:

**Geology.** — “*Facts leading to trace out the motion and the origin of the underground water in our sea-provinces*”. By Prof. EUG. DUBOIS. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Communicated in the meeting of June 27<sup>th</sup>, 1903).

As to the origin and the condition of the underground water in our low-lands, we are, as yet, almost entirely in the dark; facts, that might throw light on the subject, are almost entirely lacking.

The hazardous suppositions made on the subject by some, and the extraordinary caution, which others thought necessary in practice, prove this. Only lately DARAPSKY, in a dictatorially written article, held forth that even now rivers of former geological periods follow their very same channels, but now as underground streams. The underground water he considered as almost exclusively river-water<sup>1)</sup>.

Others have admitted powerful artesian currents from the eastern high-land, without any decided facts supporting that opinion. Again others fancied to have found the explanation in VOLGER's hypothesis, on the condensation of vapour in the ground; a hypothesis, refuted already a long time ago by no less an authority than HANN<sup>2)</sup>. A single phenomenon observed in one of the East-Frisian Islands, already years ago observed in our own country, and explained, but now forgotten, led some to imagine possibilities, as to the sea threatening us also from below, a thing which filled them with anxiety. Not to mention altogether absurd and physically impossible suppositions.

However it appeared to me that an earnest searching for facts, could not but bring to light something that would give us a clue, further to find our way in this important question, important both in a scientific and a practical respect. Indeed, thanks to the kindness I met from different sides, I was enabled, during these latter months, to make a large number of observations and to collect facts which show forth, in outline, the direction, the origin and the general condition of the underground water in the main part of our low-lands.

Since it will take some time fully to work out the results obtained, the present circumstances make it desirable I think, already now, in this short communication, to make known the most important of

<sup>1)</sup> L. DARAPSKY, Die Trinkwasserfrage in Amsterdam. Journal für Gasbeleuchtung und Wasserversorgung, 46 Jahrgang, p. 468, sqq. (1903).

<sup>2)</sup> J. HANN, Zeitschrift für Meteorologie, 1886, p. 482—486,

them. My researches were principally limited to the southern part of the North-Holland low-lands, including the dunes, and the adjacent parts of the provinces of Utrecht and of South-Holland. It is a matter of course that also here I had to limit myself to the chief points of the question.

In the last decennia, hundreds of borings have been done in the polders, in the dunes and in the area between them by the corps of military engineers and by others, with the object of making fortifications or of obtaining fresh water. Down to a certain depth, the constitution of the soil is consequently pretty well known, and some deeper borings have tolerably well acquainted us also with the constitution of the soil at greater depth. Sand is the chief substance, alternating with beds of always very impure clay. Close to the surface, pretty generally, a zone is found of clayey substances, (the well-known "old sea-clay" of STARING), over considerable areas, covered with a layer of peat, which clay, in the dunes, where that peat is generally lacking, is covered with blown sand. Under the finer sand of the upper-soil, often mixed with clay, in which occur, in large areas, deeper layers of peat, there is a zone of coarse-grained, often gravelly sand, not unfrequently containing pebbles. In the west of the mentioned region, the top of that zone lies about 30 M. ÷ A.P. deep, or a few metres higher; in the east, near Aalsmeer, Sloten, Amstelveen, Mijdrecht, Wilnis, Oudhuizen, it rises to 16 or 14 M. ÷ A.P.; near Muiden and Nigtevecht as high as 10 or 8 M. ÷ A.P. and its reaches the surface further east. Under Amsterdam and both south-east and north-east of it, the soil, on the whole, is much richer in clay.

Also at greater depths, clay-beds occur, but never as unbroken layers, extending over great distances; the most regular zone is after all that of the so-called old sea-clay, near the surface. It is besides of importance, that near our eastern frontiers much older formations come to the surface, than have been found, some hundreds of metres deep, under the lowlying lands in the west. This in itself is a reason not to expect artesian water, from Germany, in our western sea-provinces, to some hundreds of metres below the surface, at least.

Of great significance for the problem is also the fact that more or less pure clay rarely occurs. What is considered as such, on further examination, (washing of a number of samples of different origin, and especially chemical analysis, which analysis Dr. N. SCHOORL was kind enough to do at my request) proved to consist for only one third of clay at the most, generally for much less, even for only

one seventeenth. The investigations by Prof. SPRING<sup>1)</sup> have proved the fact that, and the reason why, even very thick layers of impure clay, e. g. the *limon supérieur de la Hesbaye*, let through water. What then must we think of our clay, which, though technicians will call it impermeable or "rich clay", likewise, for the greater part, consists of sand!

The chemical analysis of specimens of the fattest clay-sorts selected from their outward look, (a large number of such specimens being at my disposal from a variety of borings) showed the real clay percentage to consist of less than *a third*: at Sloten (boring IV. 2, at 4 M. ÷ A.P.) and at Uitgeest (Station, at 43 M. ÷ A.P.). Of about *a fourth*: at Hoofddorp, Haarlemmermeer (at 6 M. and also at 34 M. ÷ A.P.); at Amsterdam (Dairy at the Prinsengracht, at 9 M. ÷ A.P.) and in the dunes, 3 K.M. west of Santpoort (at 40 M. ÷ A.P.). Of about *a fifth*: at Amsterdam, (Dairy in the Second Spaarndammer Dwarsstraat, at 3.5 M. ÷ A.P.); at Harlem (Hagestraat, at 14 M. ÷ A.P.); at Hillegom (Treslong, at 14 M. ÷ A.P.); at Beverwijk (Middle of Breestraat, at 19 M. ÷ A.P.); at Alkmaar (Station, at 22 M. ÷ A.P.); in the northern part of the Watergraafsmeer polder (near the Ooster-railroad, at 35 M. ÷ A.P.); at Katwijk (875 M. South-West of the water-tower of the Leyden waterworks, at 1.6 M. ÷ A.P.). Of about *a sixth*: at Sloten (boring III. 1, at 5.50 M. ÷ A.P.) and at Eertdenkoning, in the west of the Haarlemmermeer polder (at 19.5 M. ÷ A.P.). Of about *a seventh*: at Velsen (near Rosenstein, at 2.50 M. ÷ A.P.); at Katwijk (in the same borings, at 3.8 M. ÷ A.P.). *An eighth to a ninth*: at Beverwijk in the same borings at 5 M. ÷ A.P.); at Amsterdam (Prinsengracht, at 6 M. ÷ A.P.) and in the Koningsduin near Castricum (at 32 M. ÷ A.P.). Of less than *a tenth*: at Driehuis (Nunnery, at 18 M. ÷ A.P.). Of about *a fifteenth*: at Amsterdam (Second Spaarndammer Dwarsstraat, at 62 M. ÷ A.P.); at Hillegom (Treslong, at 4 M. ÷ A.P.). Of about *a seventeenth*: in the Watergraafsmeer polder (at 8 M. ÷ A.P.). No clay at all, at Amsterdam (Second Spaarndammer Dwarsstraat, at 43 M. ÷ A.P.). The last specimen, looking like fine-sandy clay, proved to consist of sandy calcareous tufa with 77%  $\text{CaCO}_3$ .

As to peat, experiments have shown to me that its impermeableness

<sup>1)</sup> W. SPRING, Quelques expériences sur la perméabilité de l'argile. Annales de la Société géologique de Belgique. Tome 28, p. 117—127 (1901), and: Recherches expérimentales sur la filtration et la pénétration de l'eau dans le sable et le limon. Ibid. Tome 29, p. 17—48, 1892). Compare also the report of H. RABOZÉE on those investigations in: Bulletin de la Société belge de Géologie, de Paléontologie et d'Hydrologie. Tome 16, p. 269—295, (1902).

is equal to that of sandy clay, but that in another respect, it is very different from clay, i.e. in its water-containing capacity. Whereas clay, like sand, can contain water for scarcely more than a third of the volume of the dry substance, non-compressed peat can do so many times over. Peat of the Rieker polder, near Sloten, on the territory of the military water-works, was found to have a capacity of holding water, nine times the volume of the dry peat; and the water in it can, although slowly, yet freely move.

On the whole we have to deal with an upper-soil of finer, often clayey sand water, and on which or in which, in most places, enormous water-reservoirs occur: the peat beds, for even the compressed peat contains still a large quantity of water. In the colder (rainy) seasons the upper peat layers are not only always kept filled with fresh water, but they can, though slowly, provide lower regions from their water-store; and along with the water, no doubt with carbonic acid, which deep below will dissolve iron and chalk; and methane which, in the same way as carbonic acid, the more easily dissolves, the higher the pressure is. Deep down the latter product of decaying organic matter, cannot be formed, on account of the absence of bacteria.

Those upper-layers, little permeable, more or less shut off the zone of gravelly coarse-grained sand which at the bottom, in a similar way but much more imperfectly, in its turn is shut off by the irregular beds of impure clay and fine-grained sand, occurring there. Under those conditions the *vertical* motion of the water, must on the whole be difficult; at one place more and at the other less, according to clay or sand locally prevailing and in proportion to the latter being finer- or coarser-grained, whereas in the coarse-grained medium zone or zones, *horizontal* motion is comparatively easy; that medium zone is therefore the great channel, and in extracting underground water this "water-vein" is generally found at about 30 M. ÷ A.P. or a little deeper still.

That indeed below that depth the underground water has an easy horizontal passage, appears from the fact, that the height to which the water ascends in tube-wells, driven below the upper-edge of the coarse-grained bed, falls but little; whereas higher up in the fine-grained sand, it nearly always is considerably higher, (i.e. excepting the deep polders, where the deep water will naturally rise above the surface of the soil).

As to fixing the direction in which the deep underground water moves, a thing that will enable us to inquire after the existence of those currents, supposed by some, and also the origin of the underground

water, the means to do so, although hardly ever applied, are evident. Just as on the surface, it is the law of gravitation that also deep below, gives to the water its horizontal course. The direction of that motion, as caused by gravitation, can be demonstrated from the inclination of the pression-line of the water, deep below, for that motion can happen only from spots under greater, to those of smaller pression. The vertical motion, under any given constitution of the soil, can, as a rule, be inferred from the positive or negative character of the pression below, with respect to the level of the water on the surface.

When the water from the underground, freely rising in a tube-well, remains below the level of that in the upper soil, that vertical motion can take place only in a downward direction — if at any rate, then and there, a motion in a vertical direction on the whole is possible, which is mostly the case. When, on the other hand, the level of the water, in the tube-well rises higher than that of the surface-water, as is the case in the deep polders, vertical motion in a somewhat permeable soil, can take place only in an upward direction. The quantity of chlorides in the water, determined as chlorine, furnishes us with an other indication of the direction of that vertical motion.

So the observation of the height to which the water ascends in the tube-wells and the mutual comparison of the same, can teach us much as to the direction in which the water moves. A great number of those observations have enabled me to ascertain, that also deep below, the motion of the underground water (uninfluenced though it remains by small irregularities), depends on the shape of the surface. In short, the direction is from the dunes to the lower regions; from the higher to the deeper polders, and any great unevenness of the surface, makes its influence felt, already at a considerable distance. In the dunes the deep underground water is under the highest pressure; in the deepest polders it ascends in the tube-wells to a level some metres lower, although there it wells up above the ground. Near a low-lying polder the water falls also in very deep wells. So not only near the surface, but also deep below, there is a motion from the dunes to those polders and also from the higher to the lower polders.

Before communicating the observations, on which those results are founded, I must specially state, that there are influences, which for a time may more or less change the pression of the water in the underground, as it appears from the rise or fall in the wells. In the first place must be mentioned: rains, which make their influence felt

almost immediately, which influence is far more powerful than any other. After the heavy rains in the fourth week of April 1903, a number of deep wells on being sounded (April 27<sup>th</sup>) showed a higher level of 0.18 to 0.20 M. A week later it had sunk about 0.06 M., and only after the dry latter half of May, towards the end of that month, it was again what it had been towards the end of April, before the heavy rains. The rising of the deep well-water, immediately after much rain, may be in part the result of the greater pressure of the upper-soil. In the same way, a train passing over the railway-dike in the Watergraafsmeer polder, for a moment raised the water 7 m.m. in a deep well, at a distance of 18 M., which well was 34.5 M. beneath the surface of the polder. Principally the rain will increase the hydrostatic pression. In the second place, changes in the pression of the atmosphere have a passing influence on the level of the water in deep wells. Those changes make themselves felt at once, but that natural barometer is an imperfect one; the effect of the changes in the atmospheric pression soon disappears. For some hours however millimeters rising or falling of the quick-silver have their equivalent in centimeters on the watergauge.

In the third place the low and the high tide of the sea, exercise a negative or a positive pression on the deep underground water, i. e. on those spots, which are not too far from the sea (3 or 4 K. M. seems to be the utmost limit here). I have always taken those circumstances in to account. For the rest, as far as necessary, the dates of the observations are stated here. With a few exceptions, I myself ascertained the level of the water (with respect to N.A.P., the new water-mark of Amsterdam, as a standard) or it was done under my control: some other results I hold from reliable sources.

In the dunes now, the pression of the deep underground water ascends to about 3 M. above A.P. So on March 30<sup>th</sup> 1903, in a well of the Harlem waterworks sunk down to 53 M.  $\div$  A. P., situated in the midst of the dunes, at 3 K. M. west of Sandpoort, and a little further from the polderland, the level of the water was observed to be at 2.91 M.  $+$  A. P.; in another well in the dunes, deep 45.5 M.  $\div$  A. P., almost 2 K. M. further south, and at a distance of  $2\frac{1}{2}$  K. M. from the polderland, the water ascended to 2.19 M.  $+$  A. P. In a third well, close to the water-tower near Overveen and 1 K. M. from the low-lying lands, as deep as 54 M.  $\div$  A. P., it rose only to 1.20  $+$  A. P. Those three wells are at a distance of  $2\frac{1}{2}$  to 3 K. M. from the sea. In another well, near to the Brouwerskolkje, sunk down to 70 M.  $\div$  A. P., (in 1890), at  $\frac{3}{4}$  K. M. from the one near Overveen and less than  $\frac{1}{2}$  K. M. from the low-lying land, the water had been seen to ascend to

0.30 M. + A. P. The boring-hole, although still in the dunes, being comparatively low, the water rose here above the ground. The fact that those four wells are situated in the dunes, together with their comparative distances from the lower regions, distinctly make their influence felt here.

Nearer to the inland dunes, the level of the water is everywhere lower than in the middle. On the 11<sup>th</sup> of April 1903, in the Koningsduin near Castricum, the level of the water in two wells, sunk down to 32 M. ÷ A.P., was 1.195 and 1.23 M. + A.P. They were at a distance of about  $\frac{1}{2}$  K.M. from each other and they were  $\frac{3}{4}$  K.M. from the low-lying land; the distance from the sea being  $2\frac{1}{2}$  K.M. On the same day the level of the water was 0.29 M. + A.P., in a well, deep 33 M. ÷ A.P., near Santpoort, at the inland of the dunes and 2200 M. from the Zuid-Spaarndam polder (the level of the superficial water or the Summer Level here being 2.60 M. ÷ A. P.), whereas it reached no higher level than 0.055 M. + A.P. at Rosenstein, separated from the dunes by the plain of Driehuis, and only 1300 M. from the Noord-Spaarndam polder, (of the same depth as the polder of Zuid-Spaarndam).

Just as in the Brouwerskolkje near Overveen, the water rises above the boring-hole also near Bergen, on the grounds of the Alkmaar waterworks, in wells, only about 20 M. ÷ A. P. deep, for the reason of the dunes having purposely been lowered. Here however, in the midst of high dunes and at  $\frac{3}{4}$  K.M. from rather shallow polders (summer-level ÷ 1.33M.), it rose to a level of 1.35 M. + A.P., on March 1<sup>st</sup> 1903.

In a well, deep 40 M. ÷ A.P., on the grounds of the paper-manufactory of the firm VAN GELDER & SOONS, at Velsen, which well is situated at 1300 M. from the Noord- en Zuidwijkermeer polders (having 2.40 M. ÷ A. P. Summer-Level) the water on April 14<sup>th</sup> 1903, had a level of 0.26 M. + A. P. without, for 53 hours, there having been any pumping, neither there nor at any of the other wells. Under meteorological conditions which admit of comparison, a well, deep 44 M. ÷ A. P., near the small steam-mill, in the Meerweiden, on the North-Sea Canal, had a level of 0.435 M. ÷ A.P., it being situated only 370 M. from those polders and between two shallower ones (÷ 0.50 and ÷ 1.40 M. Summer-Level). In the Zuidwijkermeerfort, situated in the polder of the same name, a well, 45 M. ÷ A.P. deep, had on March 8<sup>th</sup> 1902 a level of about 0.80 M. ÷ A. P. Here we distinctly see the lowering of the level of the water in deep wells, from the dunes to the polders, which shows a horizontal motion in that direction.

The same appeared, still more distinctly, south of Harlem, through the influence, which the extensive Haarlemmermeer polder, with its outlying polders, eastward, has on it; the summer level of those polders, which together cover 42000 H. A., being about 5 M. or more under A.P.

At Aerdenhout a well, 32 M.  $\div$  A.P. deep, showed a level of 0.52 M.  $\div$  A.P. on May 5<sup>th</sup> 1903. We may admit that at the time the level of the other wells was being ascertained, it must have been here about 0.40 M.  $\div$  A.P. This well is 3600 M. from the Haarlemmermeer polder and only 350 M. from the Veenpolder (Summer-Level  $\div$  0.75 M.). A well at Heemstede, on Kennemeroord, deep only 26.3 M.  $\div$  A.P.; but sunk down into the gravelly sand, had on June 2<sup>nd</sup> 1903 a level of 0.575 M.  $\div$  A.P. That well, although in the inner-dunes, lies only 2200 M. from the Haarlemmer polder. Another well, some 100 M. north of the Common-Hall at Heemstede, at about 1300 M. from that polder and still in the inner dunes, had on May 29<sup>th</sup>, a level of 0.78 M.  $\div$  A.P. In a third one, nearly 30 M.  $\div$  A.P. deep, situated within the precincts of the community of Heemstede, but at only 440 M. from the Haarlemmer polder, on Bosbeek, at the border of the inner dunes, and under meteorologic conditions admitting of comparison, the level of the water was 1.29 M.  $\div$  A.P. A well on the Leyden Canal, deep 32 M.  $\div$  A.P., near the remise of the Harlem Electric Tram, on April 9<sup>th</sup> 1903, had a level of 0.225 M.  $\div$  A.P. This well, within the Veenpolder (Summer-Level  $\div$  0.75 M.), lies one side at 3700 M. from the encircling canal of the Haarlemmermeer polder, but also at only 1400 M. from the Noordschalkwijk polder, (Summer-Level  $\div$  1.25 M.) and the other side about 1 K.M. from the dunes. A well near the Harlem Gas Works, in the Veenpolder ( $\div$  1.40 M. Summer-Level), 1700 M. from the encircling canal of the H.M.P., had, on March 31<sup>st</sup> 1903, a level of about 1.00 M.  $\div$  A.P., and in a well on the grounds, reserved for the Harlem Abattoir, the level on April 4<sup>th</sup> was 1.08 M.  $\div$  A.P. This well lies in the Roomolen polder (Summer-Level  $\div$  1.25 M.), at 1300 M. from the encircling canal of the H. M. P.

On the other hand in a well at Hillegom (behind the building of the Hillegom Bankvereniging), sunk down to 39 M.  $\div$  A.P., 1200 from the Haarlemmermeer polder, the level of the water on April 8<sup>th</sup> 1903 was only 1.20 M.  $\div$  A.P. Although equally far from that polder as the well near the Common-Hall at Heemstede, the distance that separates this well at Hillegom from the central range of dunes, being 2900 M.; that at Heemstede only 1650 M. The upper-soil moreover at Hillegom is much richer in clay than that at Heemstede, the deep underground water consequently on the first

mentioned spot, being much more under the influence of the pression which makes itself felt in the H. M. polder.

At only 1125 M. north-east of the well at Hillegom, but 300 M. within the Haarlemmermeerpolder, at "Eert-den-Koning", a well has been sunk down to 26.3 M.  $\div$  A. P., in which on April 21<sup>st</sup>, (before the heavy rains of the last weeks of that month), the level of the water was 2.57 M.  $\div$  A. P. The cause of such a difference is some 1500 M. greater proximity of the centre of the Haarlemmermeer polder. In the midst of that polder, at Adolfshoeve, on the east Hoofdweg, 890 M. southwest of the Vijfhuizen Dwarsweg, I saw the water ascend only to 4.70 M.  $\div$  A. P. in a well, deep 34 M.  $\div$  A. P., sunk down below a bank of clay, slightly less deep. Probably the rains of a few days before, had raised the water a decimeter above its dry weather level. At Hoofddorp I found on May 8<sup>th</sup> 1903 a level of 5.03 M.  $\div$  A. P., in a well only 18.5 M.  $\div$  A. P. deep. Although less deep than the other wells, also this was sunk into the less fine sand, and near the top of the coarse-grained sand, beneath the less permeable upper-soil of fine sand and clay. If the well had been sunk below the clay-bank and 34 M.  $\div$  A. P. deep, the water no doubt would have risen a little higher. So the result is, that in the midst of the Haarlemmermeer polder, the underground water, from under the deeper lying clay, can ascend half a metre above Summer Level (this being 5.20 M.  $\div$  A. P.), on the other hand, from under the clayey top-layer, it can rise but little above it. The pression it acquired in the dunes and in the surrounding, shallower polders, on its way to the H. M. polder, is in the middle of it, at 18.5 M.  $\div$  A. P., almost entirely lost; and at 34 M.  $\div$  A. P. reduced to about half a metre, so it can rise but little above the surface underground water, whereas at "Eert-den-Koning", the ascending capacity of the water rising from 26 M.  $\div$  A. P. is 2.63 M. above Summer Level, or about 1.50 M. above the grass-land of the polder. The upper-soil, we must bear in mind is half permeable, and on its way to the middle of the polder, the water gradually loses more or less its ascending-capacity. Consequently also, the water cannot horizontally move further east, for then it would have to move to parts, where there is more pression.

That indeed the difference in pression between the surrounding higher parts and this deep polder, is the cause of the motion, appeared from observations taken on other spots round the Haarlemmermeer polder, and in the deep polders more east, adjacent to it, including the large Mijdrecht-polder.

North-east of the Haarlemmermeer polder, in the Ricker-polder,

a great many wells have been sunk for military purposes, most of which wells are about 50 M.  $\div$  A.P. deep. The levels in them were repeatedly sounded by me, which, considering their large number, led to important results. Specially of great significance is what those soundings teach us, as to the direction in which the deep underground water moves. Subjoined table, in which, as much as possible, only wells of corresponding depths have been put down, entirely confirms what I found elsewhere.

Those soundings were done on June 5<sup>th</sup> 1903. The distances of the wells to the H.M.polder itself, one will get by adding 80 M. to the figure that expresses the distance between them and the encircling canal.

Number of the well.	Depth, in M. $\div$ A.P.	Distance in M., to the encircling canal from the H. M. P.	Level of the water in the well, in M. $\div$ A.P.
II. 8	56.5	25	3.00
I. 19	47.0	50	2.99
20	49.8	75	2.985
21	45.6	100	2.995
III. 1	47.2	367	2.94
10	55.7	525	2.91
21	51.5	750	2.835
23	52.3	795	2.83
25	52.9	840	2.82
35	55.0	1090	2.81
36	54.0	1120	2.80
37	50.6	1145	2.80
40	52.8	1225	2.78

Here clearly comes out a motion of the deep underground water, from the higher polders, north of the Haarlemmermeer polder, towards this deep polder. On 1200 M. of distance there is an inclination of 0.22 M., or 1,8 : 10000, whereas in other directions, there is no regular inclination. That indeed no general motion from east to west or vice versa is to be thought of, naturally follows from the comparison between the level of the water in wells thus situated. For instance from the following row of wells, all at 25 M. from the encircling canal of the H. M. polder.

Number of well.	Depth in M. ÷ A.P.	Distance in M. from well II. 5.	Level, in M. ÷ A.P.
II. 5	56.3	0	3.025
6	39.0	50	2.98
7	40.1	100	2.98
8	56.5	150	3.00
10	46.5	250	2.99
12	33.5	318	3.005
14	44.0	380	3.025
I. 18	38.0	595	3.01

At the same time the fact stands forth that, once a level reached under the fine-grained and clayey upper-strata, further differences in depths are of little consequence.

Comparison of the other soundings will show forth the same for either statement.

The average level of last mentioned 8 soundings, in wells at 25 M. distance from the encircling canal, is  $\div 3.00$  M., so equal to that in well II 8 which we used as starting-point in the first table.

Though there is no great current in the one or the other direction, vertical on the one towards the H. M. polder, (so from east or west,) there seems to exist a slight local motion from the Nieuwe Meer (level about  $\div 0.60$  M.) to the west (Summer Level of Rieker polder  $\div 1.80$  M.), as may be seen from the comparison between wells, situated at increasing distances from that small lake, but pretty well at an equal distance from the H. M. polder.

Number of well.	Depth, in M. ÷ A.P.	Distance in M., from the N. Meer.	Level, in M. ÷ A.P.
I 1	48.5	60	2.935
2	48.7	90	2.935
3	50.5	110	2.925
4	51.0	135	2.932
7	52.8	220	2.955
8	51.5	235	2.95
9	50.0	235	2.955
10	49.5	235	2.96
12	41.3	300	2.98
II 14	44.0	690	3.025

The real existence of the above indicated motion, from the shallow polders, north of the H. M. polder, towards the latter, is confirmed by observing the level in a well, sunk down to 32.5 M. ÷ A.P. under the direction of Dr. ALEXANDER KLEIN, near the "Huis de Vraag", between the Rieker polder and the Slotter Binnen- and Middelveldsche combined Polders (Summer Level ÷ 2.15 M.), not far behind the Vondel Park. On June 16<sup>th</sup> 1903, I found the level to be 2.46 M. ÷ A.P. The well lies 3100 M. from the H. M. polder, or about 1800 M. further than well H $\ddot{F}$ . 40, in the Rieker polder. So also here there is an inclination of about 1.8 : 10000.

Also towards the polders which lie eastward, adjacent to the H. M. polder, and hydrologically one with it, the motion of the water, deep down, is from the higher to the lower ones. This was shown by soundings, done on June 24<sup>th</sup> 1903, in wells, all sunk down to about 30 M. ÷ A.P. and belonging to fortifications south-east of Amsterdam. There appeared to be an impelling force in that deep water towards the Groot-Mijdrecht polder (where they keep the water to a Summer Level of ÷ 6.60 M.).

The following small table, concerning observed levels on August 26<sup>th</sup> 1903, shows this :

	Distance to the Groot-Mijdrecht Polder	Level. in M. ÷ A.P.
Fort near Nigtevecht	7 KM.	1.775
Mil. Post near Oostzijdschen Watermill	5.5 „	2.01
Fort near Abcoude	4.5 „	2.12
„ „ De Winkel	2.5 „	2.29
„ „ Botshol	0.2 „	4.43

The fact that the inclination of the pression-line is specially great here, near the deep polder, and also from Nigtevecht to the Oostzijdschen Watermill, must, I think, be attributed to the greater height to which the gravel-diluvium rises in this part, a thing to which attention has been called, already at the beginning of this paper. The influence of surface-water can therefore make itself felt comparatively strongly, when locally rapid changes occur ; at Botshol, on account of the neighbourhood of the deeper polder, and at Nigtevecht on account of the rising of the upper-part of the deposit of coarse grained sand, which at a comparative small distance, east of Nigtevecht, at certain spots, even reaches the surface. The reason being that the artesian regularity of pression, to which the deep

underground water is submitted, is broken by those local irregularities of the geological structure.

That we have not to think of strong currents of the deep underground water, in a general direction for all, but of currents, dependent on the local form of the surface, may finally be confirmed by soundings in two wells, sunk also under the direction of Dr. KLEIN, in the Watergraafsmeer polder (Summer Level  $\div$  5.50 M.). One of those wells, in the north of that polder, near the Ooster-railway, at 250 M. north-west of the so called Poort, deep about 39.5 M.  $\div$  A.P., had on June 18<sup>th</sup> 1903 a level of 3.215 M.  $\div$  A.P. In another, presumably 35 M.  $\div$  A.P. deep, in the south of that polder, near the Omval, the level was 3.125 M.  $\div$  A.P., on June 23<sup>d</sup> 1903. The latter lies 5 K.M. almost straight east, from that near the "Huis de Vraag," which in its turn lies 2.3 K.M. east, but a little towards the north, from well III. 40, in the Rieker polder.

Another well, about 25 M.  $\div$  A.P. deep lies, in the south-west corner of the Bijlmermeer polder (Summer Level  $\div$  4.80), at 4 K.M. north-west of the well near the Oostzijdschen Water-mill, 4.8 K.M. south-east of that near the Omval and 11 K.M. from the Bullenwijker and Holendrecht polder (Summer Level  $\div$  3.35 M.). This well had, under the same meteorological conditions, a level of 3.075 M.  $\div$  A.P. At the well-known boring done by the corps of military engineers, at Diemerbrug, near the Weesp turnpike, beyond the northern extremity of the Bijlmermeer polder, the level of the water in the well, then 73 M.  $\div$  A.P. deep, was 2.51  $\div$  A.P. on Oct. 18<sup>th</sup> 1888. That well was 2 K.M. from the eastern border of the Watergraafsmeer polder.

Consequently the result of the different observations is, that there is not a general, so called "artesian" current from east to west or vice versa, in the region between Amsterdam and the H. M. polder, neither south-east of Amsterdam; those found, are but special currents originating in local differences of height of the surface and directed towards the Haarlemmermeer- and adjacent other deep polders and towards the Watergraafsmeer-, the Bijlmermeer- and the Holendrecht polders.

Another result is the conclusion we may draw, as to the direction of the vertical motion of the underground water, by comparing the different levels of the water in the deep wells with that of the varying levels of the underground water rising from smaller depths and with the highest level this reaches. In short in the shallow polders, in the dunes and in the area between them, the direction appears to be downward; in the deep polders, on the other hand,

such as the Haarlemmermeer polder and the adjacent deep ones, upward. It is a wellknown fact that the water in deep wells rises above the surface of the underground water and above the grassland of the deep polders. In polders of smaller depth, the deep wellwater remains below the surface. Likewise the ascending power of the water, as a rule, gradually diminishes towards the middle of the deep polders. In higher parts, such as in the dunes and in the flat sandy adjacent area, the surface of the underground water is considerably higher than the level of the water in the deep wells. So here we find increase of pression from below upward, and descending movement of the water. In the dunes near Castricum the level of the surface of the underground water is about 1.30 M. higher than that reached in the deep wells; at Santpoort, at the inland side of the dunes, the difference even being 1.80 M.

In connection with the above indicated conditions, especially in the colder seasons, when the underground water is generally fed with the water penetrating the soil from the rainfall, the dunes, the shallow polders and the intermediate area will get a fresh supply of water, whereas there is always a loss by the pumping in the deep polders, to which, certainly in no less degree than to the sea, there is a constant affluence. The underground water not being of distant origin, it can as a matter of course be derived only from rains on the spot itself, or at a small distance.

Just a passing remark in connection with the results arrived at, to call the attention to the drying out of the dunes and especially of the lower stretches of land west of the H. M. polder. This drying out, i.e. considerable lowering of the surface-level of the underground water, actually noticed for already half a century, has repeatedly been attributed to the waterworks in the dunes for the water-provision of Amsterdam: to my opinion however it is in the first place due to the draining of the Haarlemmermeer, just half a century ago, from which event dates the powerful subterranean current from the dunes to the deep extensive Haarlemmermeer polder. Especially in the lower tracts from Zuidschalkwijk to Bennebroek, up to a few kilometers from that polder, the drying out process has made itself felt, on account of clay above the coarse-grained sand being almost entirely lacking. In those parts the water in the ditches, when there is no fresh artificial in-flow, will soon sink down, actually making its way under the encircling canal of the H. M. polder, as is proved by the considerably lower level in part of

that region <sup>1)</sup>. Ever since, a few years ago, the level of the H. M. polder was lowered 0.30 M., the level of the water in a pond, 4 M. higher, at Meer-en-Berg, and 400 M. outside the polder, was observed to be lowered as much. From this we can imagine how powerful the influence of a lower level of 5 M. must have been at the time when the Lake of Harlem was being drained dry.

As to the motion of the deep underground water, at the side of the dunes, facing the sea, I have been able to make only a few observations. The great uniformity with which the dunes border on the sea however, in connection with the other results of my investigation, permit drawing pretty safe conclusions from them, as to the general condition.

A well known fact is that the superficial water flows from the dunes towards the sea, just as it does inland from the dunes to the adjacent flat area and the polders. A remarkable proof of the water flowing from the dunes to the sea, is the welling up, at ebb-tide, of fresh water on the beach, north of Noordwijk-aan-Zee. Puddles and furrows form themselves, from which, as long as it is ebb, not unlike rills, fed from sources, large quantities of water, only partly consisting of salt-water, flow towards the sea. Particles of clay brought up with the water and found in the ripple-marks on the beach, suggest the presence of a clay-bed, close to the surface, through interruptions of which the welling up of the water takes place. On March 27<sup>th</sup> 1903, at 11 a.m., it being low-tide, about 9 hours after high-tide, (the wind S.S.E.), I scooped opposite strand-pole N<sup>o</sup>. 78, from such a rill, about 200 M. long, (the debit of which might be calculated to be in the least 7 M<sup>3</sup> an hour), a sample of water, which proved to contain 11550 mG. of chlorine the Liter. So for  $\frac{1}{3}$  it was fresh- and for  $\frac{2}{3}$  sea-water, and hourly more than 2.3 M<sup>3</sup> fresh water found its way into the sea, through that little ebb-rill. The great uniformity now with which the dunes slope down to become beach permit us to accept as a general though in most cases invisible fact what here, through local circumstances, happens visibly.

Another proof for the considerable flowing down of fresh surface-water towards the sea, furnished to me a stone-well at the foot of the dunes, on the beach at Zandvoort, from which the fishing-smacks take their water-store. The bottom of that well is 0.72 M.  $\div$  A.P.,

<sup>1)</sup> That also from the encircling canal itself, which is about 3 M.  $\div$  A.P. deep, the water is sinking down, is proved by the fact, that near the Cruquius, the level is always some centimeters lower than in the Spaarne and in the canals of Harlem.

i. e. 0.04 M. above average low-tide mark, and 1.250 M. below high-tide mark. On Febr. 18<sup>th</sup> 1903, at 4.20 p.m., it being low-tide, the quantity of chlorine of the water in that well, was 291 m.G. the Liter. On March 6<sup>th</sup> 1903, at 10.30 a.m., about three hours after high-tide, the level of the water in that well was 0.93 M. + A.P. or 0.76 M. above the sea, at that moment.

Also in the deeper, coarse-grained sand-layers, there is a main current of fresh water towards the sea. In a well in the dunes, 350 M. from the sea (low-water line), on the Kerkplein at Zandvoort, sunk down to 28.3 M. ÷ A.P., the level of the water on the 14<sup>th</sup> of April 1903 was as follows :

At 4.30 p.m.	1.445 M. + A.P.
.. 5 .. ..	1.497
.. 5.25 .. ..	1.520

So a distinct influence of the high-tide, which at IJmuiden reaches its highest level, 1.43 M. + A.P., at 4.55 p.m.; at Zandvoort presumably 8 minutes earlier, is evident.

The next day, in the same well — the deeper one of the two — the level of the water was found to be :

At 12 o'clock	1.28 M. + A. P.
.. 12.35 p.m.	1.24
.. 1. 5 .. ..	1.22
.. 1.35 .. ..	1.195
.. 2. 5 .. ..	1.19
.. 2.35 .. ..	1.193
.. 3. 5 .. ..	1.205
.. 3.25 .. ..	1.20

Comparing the above figures with those of the self-registering tide-gauge at IJmuiden, it appeared that the influence of the tide makes itself felt 40 minutes later in that well, situated 350 M. from the sea. The sudden way in which the gradual rising of the water stopped at 3.5 p. m. was found to correspond with the somewhat earlier, change in the level of the sea, the difference in time corresponding.

At IJmuiden, 1.30 p.m., the low-tide level was observed to be 0.76 M. ÷ A.P.. So the water in the well was 1.95 M. higher. At high-tide however, it was at that time, but about 0.10 M. above the level of the sea. So the amplitude of the tide influence in the well,

was then about 0.34 M. But the tide rose then unusually high (0.55 M. above the average high-tide mark) the low-tide mark being then just the average one. I think I may estimate the average vertical amplitude in the well to be, at the most, 0.30 M., and believe pretty near to hit it, when accepting 1.30 M. + A.P. as the average level in that well, or 1.50 M. above the average sea-level.

When considering the motion of the deep ground-water, in the direction of the sea, caused by the hydraulic pression in the dunes, we must not overlook the much greater specific weight of sea-water. A column of sea-water 30 M. deep, (with a specific weight of 1.0244, on the average, as that of the North-sea-water), will be kept in balance by a column of fresh water, about 0.75 M. higher. No doubt however the depth of the fresh water, in the coarse-grained sand below it, is much greater than 30 M. ÷ A.P., without any considerable decrease in the ascending power. A direct proof of this is the small percentage of chlorine of the water in the deep well in the Kerkplein, amounting only to 45 m.G. p. Liter, and that in the well on the beach, 30 M. deep, about 250 M. more south, was 52 m.G. the Liter. In statistic equilibrium, 1.50 M. above the average-level of the fresh underground water would correspond with a depth of 61.5 M. But on account of the motion of the fresh water we have here to deal with a condition of dynamic equilibrium; the pressure at great depths consequently is not simply settled by the height, to which the water ascends higher up, in the ground. However below 30 M. (in the coarse-grained sand) there will be little difference, so we cannot but accept, that an extra-pression of 1.50 M. of the sweet ground-water, apparent from the level the water reached in the tube, will correspond with a depth of about 60 M. ÷ A.P.; taking in consideration the decrease of pression downward, we may safely state the depth to be 50 à 60 M. ÷ A.P. One thing is sure, the water which rises from about 30 M. ÷ A.P., has still ascending power above the level of the sea. This may be distinctly observed in the well, sunk on the beach, although being 300 M. nearer to the low-tide line, a considerable decrease can be noticed. At that small distance, the deep underground water in the dunes has already, for the greater part, lost its ascending power and we may accept that not far out into the sea, it is entirely gone. That strong pression-fall must be principally attributed to tide-fluctuation, which every time renews a fourth of the water in the sand, as far as that fluctuation makes itself felt; apparently (the well in the Kerkplein shows it) at a rather considerable distance, from the sea. But also the fact that the beach slopes down — at Zandvoort the depth of the sea, 400 M.

from the low-tide line, being 2.5 M.; 1200 M. beyond that line. 5 M. below A.P. — and that the fine-grained sand intermixed with clay of the original upperlayers for a great part will have been replaced by coarser sea-sand, must considerably have contributed towards greatly increasing the pression-fall of the deep underground water, at the sea-side. At high-tide the flowing off however is very small, and all things considered, the flowing off of the water from the dunes, at the polderland side, certainly will not be less considerable than that towards the sea.

But let us drop this subject, too few facts being at our disposal to judge of that complicated process, and watch the influence of the sea-water at a greater distance from the coast. There can exist no doubt as to the underground of our low-lands being soaked with sea-water. In none of the borings executed in the last scores of years, if only deep enough carried through, the proof of it was lacking; more or less deep, according to circumstances, but the underground water showing an ever increasing quantity of salt, highly exceeding that of all polders ditches or canals, exceeding even that of the Zuiderzee. In or near the dunes, one must go much deeper to find sea-water, than in the polders; and in the polders, on higher ground, as a rule, deeper than in those lower situated. In the Brouwerskolkje, at a depth of 72 M. ÷ A.P., the percentage of chlorine did not exceed that of surface dune-water, neither was this the case in wells of the Harlem water-works, deep 54 M. ÷ A.P.; nor in the one, in the dunes at Elswout, 80 M. ÷ A.P. deep; nor in the Rieker polder at more than 50 M. ÷ A.P. Near the Huis-de-Vraag, in the north-east corner of the Rieker polder, down to 32.5 M. ÷ A.P. only 34 m.G. chlorine a Liter was found; at 46.5 M. ÷ A.P. not more than 81 m.G.; and near “Het Kalfje”, on the Amstel, south of Amsterdam, at 31 M. ÷ A.P., only 47 m.G. a Liter. At Purmerend, situated in shallow polders, with Summer Levels of 1.25 to 1.60 M. ÷ A.P., but surrounded by the deep Purmer- (Summer-Level ÷ 4.47 M.), the Beemster- (S.L. ÷ 4.00 M.) and the Wijde wormer polder (S.L. ÷ 4.50 M.), the water rising from 50 M. ÷ A.P., has a quantity of only 43 m.G. of chlorine a Liter. The well-water at Schermerhorn, in shallow polders, between the deep Beemster- and Schermer polders, at 76 M. ÷ A.P. deep, contains 170 m.G. chlorine a Liter. Although the underground water in those deep polders, on the whole is brackish, the quantity of chlorine was only 192 m.G. a L. in the Purmer polder, at about 1 K.M. from the encircling dike, in the direction of Purmerend on the Westersweg, and 600 M. north the church. Similar fresh deep underground

water is also found in the south-east corner of the Beemster polder, opposite Purmerend.

On the whole west of the Haarlemmermeer polder, in wells not greatly exceeding 30 M. in depth, the underground water is equally fresh as dune-water, also at Heemstede and at Hillegom and in some of the shallow polders near Haarlem. At great depth, there is in those parts a considerable increase in the quantity of chlorine. Near the railwaystation of Vogelenzang, between the Leidsche vaart and the rail-road, at 1600 M. from the Haarlemmermeer polder, at a depth of 88 M.  $\div$  A.P., it amounted to 184.6 m.G. a Liter, it being only 35.5 m.G. a Liter at 25 M.  $\div$  A.P. Near the villa Bennebroek, 650 M. from the Haarlemmermeer polder, 47 M.  $\div$  A.P. deep, it contained 99.4 m.G., and at a depth of 89 M., 245 m.G. chlorine a Liter; on Bosbeek, in the parish of Heemstede, being only 440 M. from that polder, at about 30 M.  $\div$  A.P., 58 m.G. a L. Numerous instances may be brought forward of the quantity of salt in the underground water growing with its greater depth, and at a higher level, as one draws nearer to the deep polders. A well-known fact is, that in consequence of the flowing down of the underground water from off the dunes, the water of the neighbouring low-lands, up to quite a few kilometers' distance, may be fresh. More considerable and noticeable at greater distance however, is that down-flow deep in the ground. Close to the steam-mill for the draining of the land, in the Meerweiden near Velsen, at full  $\frac{1}{2}$  K.M. from the dunes, the underground water, 28 M. below A.P., contained 30.5 m.G. chlorine and at 44 M. below A.P., 65.4 m.G.; and even 1 K.M. more east, within the precincts of the fort, in the western corner of the Zuidwijkermeer polder (S.L.  $\div$  2.40 M.), at 34 M.  $\div$  A.P., only 60 m.G.; at 45 M.  $\div$  A.P., on the other hand, 603 m.G. chlorine a Liter. In the midst of the dunes themselves the ground-water seems to get brackish only at about 150 M. below A.P.

Of special significance is the fact, already stated above, that the underground water in the deep polders is growing saltier at a much higher level. So at Eert-den-Koning, only 300 M. within the Haarlemmermeer polder, at 26 M.  $\div$  A.P., the underground water had 367 m.G. chlorine a Liter. Similar conditions are generally prevailing there. That, generally speaking, the higher percentage of salt cannot be attributed to water from the canals ("boezemwater"), so cannot have got in from the surface, may in the first place, be proved from the fact, that the water in shallow polders, in many places, down to considerable depths is as perfectly sweet as that in the dunes, although one can prove that there is no communication with the dunes; in the second

place, that within those polders, just as outside them, but already at a higher level, the water deeper down will be found to have a higher salt standard. At Hoofddorp the quantity of chlorine, at 18.5 M. ÷ A.P., was 202 m.G. a Liter; at 28 M. ÷ A.P., 260 m.G. and at 38 M. ÷ A.P., 993 m.G. With such a rapid increase as in the last 10 M., unmixed sea-water may be expected, at little greater depth.

No doubt can be entertained as to underground sea-water and fresh water in our sea-provinces balancing each other in a way, as indicated by BADON GHYBEN and HERZBERG <sup>1)</sup>, very much however modified, in general and in special cases, by the general geological structure with its local modifications. There is no ground for fear of the sea-water coming up from below, in part of the dunes, in which the underground water has been lowered down to the sea-level; the very fact that there are polders, which already for centuries lie below it, and still have fresh water, down to great depths, and that even of the deepest polders the upper-soil, several scores of metres deep, is much more soaked with fresh than with salt water, refutes that fear.

Remarkable however is that at Hoofddorp, although situated in the midst of the Haarlemmermeer polder, the deep underground water is less salt than at Eert-den-Koning, near the edge of the polder, and less still so than some kilometres north-west of Hoofddorp, e. g. on the farm Mentz, where a deep well, presumably equally deep, has water containing 653 m.G. chlorine a Liter, i. e.  $2\frac{1}{2}$  times the quantity of that at Hoofddorp. Differences in the condition of the sub-soil are evidently the cause of those differences in the salt quantity.

In the shallow polders, on account of the direction downward of the vertical motion, also the water from the canals ("boezemwater") may be the cause of rendering the deep underground water salt, when locally the structure of the soil does not prevent it.

Bearing in mind, for the motion of the underground water, the significance of the different heights of the polders, and not forgetting the irregularities in the extent, the thickness and the comparative pureness of the clayey beds, also irregularities in the vertical distribution of the water and in the composition of it may be explained.

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<sup>1)</sup> W. BADON GHYBEN in: Tijdschrift van het Kon. Instituut van Ingenieurs 1889, p. 21; HERZBERG in: Journal für Gasbeleuchtung und Wasserversorgung. 1901, p. 815 s.q.q. I count myself happy to have pointed out in lectures, conversations and letters this forgotten merit of one of our engineering-officers, in consequence of which remembrance Mr. C. E. P. RIBBIUS and Mr. R. d'ANDRIMONT have, in their publications given due honours to our compatriot.

Intermixing with water, richer in salt, both from above and from below, may consequently be hindered or furthered by it, also the oozing in of fresh water; the different mixtures, as an other consequence, being able to move horizontally in the one or the other direction, or be prevented to move at all, which explains the different levels they reach.

The hypothetic currents can be dispensed with to explain the existence of fresh water, between 35 and 50 M. ÷ A.P., in the old boring at Sloten, so often urged in proof of powerful subterranean water-currents of distant origin. Of the above mentioned wells in the Rieker polder, those, most west, are only 800 M. east of the boring of 1887. The different levels observed in the wells at Sloten can in reality be due only to local motion, in the direction of the shallower polders (with their higher upper-pressure) to the deeper polders, where the pressure from above is less powerful. The fresh water, everywhere found there at great depths, down to 50 M. ÷ A.P., can find its origin only in those shallow polders themselves. The very position of the old boring at Sloten, at a corner of the shallow Rieker polder, between two deep polders (the H. M. polder and the Middelveldschen Akerpolder (S. L. ÷ 4.20 M.)), explains the irregularities of composition observed there in the vertical distribution of water, and thus it is, with the boring near Diemerbrug, outside the north corner of the deep Bijlmermeer polder (S.L. ÷ 4.20 M.). At about 250 M. ÷ A.P. water of a somewhat lower standard of salt (minimum 1192 m.G. a Liter) was found; no fresh water, as DARAPSKY lately held forth. Considering what influences are at work in the distribution of the water in our soil, one can but see natural phenomena in all those deviations.

Considering the geological condition of the place itself and of its surroundings, the occurrence at Wijk-aan-Zee, both of fresh water down to 31 M. ÷ A.P. (47.8 m.G. chlorine) and of its getting brackish, already at 50 M. ÷ A.P. (351 m.G. chlorine) may be easily explained; also the presence of a layer of fresh water, between the sea-water, in the sub-soil of IJmuiden.

In this discourse on some general features of the movement of the underground water in our lowlands the question remains to be settled, how it is that some shallow polders, of which the canals and the ditches like those of other, deeper polders, are mostly filled with brackish water, can furnish fresh underground water.

In the first place the answer will be that, by no means, all surface waters of the polders are brackish. Even in the H. M. polder, I found, also at dry seasons, in some places fresh surface water

containing only 78, 60, 35.5 mG. of chlorine a Liter. Holes made in the midst of deep-polder meadows often fill with fresh water, even when a long period of absolute dry weather precedes the digging of them; so in the Purmer-polder, near the above mentioned deep well, on May 13<sup>th</sup> 1903, the water in such a hole, dug about 1.80 M. deep, contained only 72.6 m.G. chlorine a Liter, the adjacent ditch water having 407 m.G. Near Hoofddorp, in the H. M. polder, in the midst of the Slaperdijk, 250 M. southwest of the Hoofdvaart, after weeks of dry weather, in a hole, the Corps of military engineers had dug, down to 0.40 M. below polder-level, water oozed in, which contained not more than 102 m.G. chlorine a Liter, still that dike (the summit of which is about = A.P.) over all its length stretches between two canals 10 à 15 M. wide, only 40 M. apart and always filled with brackish water, 1 or 1.5 M. deep. The water of those canals at that moment contained 511 m.G. of chlorine a Liter. The level of the water that had gathered in the hole, was 0.11 M. higher than that in the canals and at that time they were even considerably higher than they had been the last month. But those are deep polders, in which the vertical motion of the underground water is from below upward. What to think now of the water that penetrates the soil of the shallow polders? The extent of the land, in the polders, generally exceeding that of the water at least 25 times, and the level of the underground water in rainy seasons, being considerably higher than the neighbouring ditch water, consequently the fresh water will filter down, in a far greater proportion than the brackish, the surface of which forming but an insignificant portion of that of the fresh water fallen in the meadows. The water of the canals ("boezemwater") consequently can but little add, in those rainy seasons, to the salt-standard of the underground water. In the dry season, on the other hand, the land drying out, water must be let in; the soil is then absorbing brackish water from the canals. In fact, however, even such shallow polders, as the Rieker polder and those of Purmerend, which possess fresh underground water below the recent more or less impermeable strata, have brackish underground water near the surface, all the year round. Nevertheless, to my opinion, a great number of phenomena point to the supposition of the deep fresh underground water, found in some of our shallow polders, which have brackish underground water near the surface, being due to rainfall on the spot itself, or at a comparative short distance. This question will be the subject of a further communication.

Considering the facts communicated here, in connection with others,

concerning the quantities of water which from the rainfall penetrates the soil, it need not be further demonstrated that in the sub-soil under the dunes, under the adjacent flat elevated area and under some shallow polders, drinkable water is and will not be lacking, in the main land of the provinces North- and South-Holland, superficially judging so little favoured in this respect, and with two fifths of the population of our country. That the velocity with which the deep underground water can move through the coarse-grained sand, is quite sufficient to make it possible to procure it from the sand in large quantities, a great number of facts prove it. I will mention but one, that of the paper-manufactory at Velsen, of which the six wells, encompassing an area of 0.85 H.A., every 24 hours, on the average, furnish at least 2200 M<sup>3</sup> of fresh water or nearly as much as the town of Harlem wants and about a tenth of what Amsterdam consumed during these latter years. And those wells furnish water, which shows no signs as yet of a too slow horizontal motion ere long being likely, by disturbing the natural equilibrium of the underground fresh and salt-water, to convert the pumped fresh into salt-water. On the contrary the water of the oldest well, full six years in use, has grown a little sweeter still.

**Physics.** — *“Investigation of a source of errors in measurements of magnetic rotations of the plane of polarisation in absorbing solutions.”* By Dr. L. H. SIERTSEMA. (Communication N<sup>o</sup>. 91 from the Physical Laboratory of Leiden by Prof. H. KAMERLINGH ONNES.)

(Communicated in the meeting of January 30, 1904).

In a great number of measurements of the magnetic rotation of the plane of polarisation it was found, that this rotation assumes very large values in the neighbourhood of an absorption-band. Similar large values were found by me in an investigation on the negative magnetic rotation of potassium ferricyanide<sup>1)</sup> in dilute solutions. These results agree with the new optical theories which yield for the magnetic rotation the dispersion formula:<sup>2)</sup>

$$\varrho = \frac{e \lambda}{m 2 V} \frac{dn}{d\lambda}$$

since the quantity  $\frac{dn}{d\lambda}$  also assumes a large value near a band.

<sup>1)</sup> Arch. Néerl. (2) 5 p. 447; These Proc. 1901/02 p. 339; Comm. Phys. Lab. Leiden N<sup>o</sup>. 62. 76.

<sup>2)</sup> These Proc. 1902/03 p. 413; Comm. Phys. Lab. N<sup>o</sup>. 82.

Much attention should therefore be paid to the fact that BATES<sup>1)</sup> has made measurements with solutions of cyanine, fuchsine, litmus and aniline blue, from which it would follow that these large rotations did not exist, whereas SCHMAUSS<sup>2)</sup> with these very substances has found very large rotations. According to BATES these large differences are caused by a source of error which arises from the circumstance that for these measurements we make use of light of which the intensity varies with the wave length<sup>3)</sup>. He shows that both with the half-shadow method, and with that where we adjust on a dark or a bright band in the spectrum, great errors may be made as soon as we arrive at a region where the intensity-curve of the light used shows a considerable decrease, and that this may produce apparently large rotations.

As this source of errors might also occur in my measurements with potassium ferricyanide, it seemed important to me to investigate in how far this may have had a disturbing influence, and thus in how far the large rotations then found would have to be ascribed to it.

With the method involving the use of a dark band in the spectrum, the source of above errors comes to this, that as soon as the intensity of the light on the two sides of the band is not the same, we are inclined to wrongly adjust the middle of the band, and to displace it too much towards the dark side. For we may suppose that for an adjustment we, as a rule, search for two points on the borders of the band which are of equal intensity and then adjust between them. It must be noted that attention has been repeatedly drawn to this source of error<sup>4)</sup> although, as far as I know, an experimental investigation of the errors which may so arise was first made by BATES<sup>5)</sup>. A theoretical solution would be possible in the manner indicated by BATES, but this requires a knowledge of the intensity-curve of the spectrum which is seen by the observer in the absence of the magnetic rotation. Moreover we ought to know which of the intensities on the edges is used by the observer to determine the middle of the band, and this especially will partly depend on the observer. An experimental determination may easily be made. We need only produce a spectrum with a movable dark band and

1) BATES. *Ann. d. Phys.* (4) 12 p. 1091.

2) SCHMAUSS. *Ann. d. Phys.* (4) 2 p. 280; 8 p. 842; 10 p. 853.

3) BATES. *Ann. de Phys.* (4) 12 p. 1080.

4) GERNEZ. *Ann. éc. norm.* 1 p. 12 (1864).

VAN SCHAİK. Thesis for the doctorate. Utrecht 1882 p. 30.

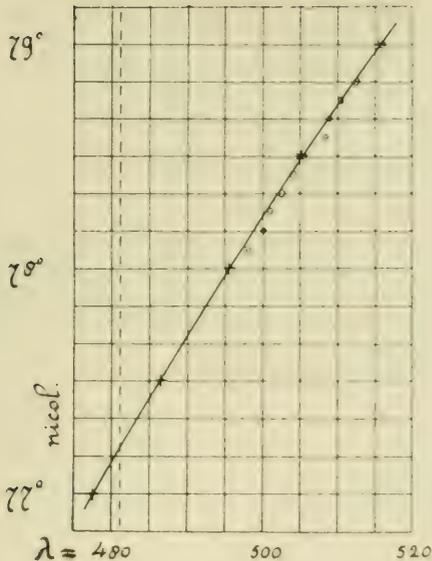
5) BATES l. c. p. 1086.

examine it while the light passes or does not pass through an absorbent substance. The apparent displacement of the band near the limit of absorption must then immediately appear.

For my measurements with potassium ferricyanide I have made use of rotations of  $11^\circ$  and higher. A quartz plate 0.4 m.m. thick, cut at right angles to the optical axis was now used and with it a similar rotation is obtained near the limit of absorption. This plate preceded and followed by a nicol was placed between the collimator and the experimental tubes, which moreover were mounted in precisely the same way as they were for measurements of the rotation in potassium ferricyanide. A large number of adjustments have been made by rotating one of the nicols, one set where the experimental tube was filled with a  $\frac{1}{2}\%$  solution of potassium ferricyanide, and one with water instead of the salt-solution. The calibration of the spectrum was made as before with a mercury arc lamp. The following values have thus been obtained, as means of pairs of adjustments:

nicol	water	band with $\lambda$ in $\mu\mu$	solution
$83^\circ 0'$	629 <sup>s</sup>		630
$82^\circ 30'$	611		612
$82^\circ 0'$	593 <sup>s</sup>		593 <sup>s</sup>
$81^\circ 30'$	577		577 <sup>s</sup>
$81^\circ 0'$	562 <sup>s</sup>		563
$80^\circ 30'$	549		549 <sup>s</sup>
$80^\circ 0'$	538		538
$79^\circ 30'$	525		526 <sup>s</sup>
$79^\circ 0'$	515 <sup>s</sup>		516
$78^\circ 50'$			512 <sup>s</sup>
$78^\circ 45'$			510 <sup>s</sup>
$78^\circ 40'$			509
$78^\circ 35'$			508 <sup>s</sup>
$78^\circ 30'$	505		505 <sup>s</sup>
$78^\circ 25'$			504
$78^\circ 20'$			502 <sup>s</sup>
$78^\circ 15'$			501
$78^\circ 10'$			500
$78^\circ 5'$			498
$78^\circ 0'$	495 <sup>s</sup>		
$77^\circ 30'$	486 <sup>s</sup>		
$77^\circ 0'$	477 <sup>s</sup>		

(limit of absorption, about 481)



- + series with water
- " " solution
- ⋮ limit of absorption

The annexed figure represents graphically a part of these readings for both sets. The irregular differences, may apparently be ascribed to errors of observation, which near the limit of absorption will be somewhat larger than at other places, owing to the smaller intensity of the light. They do not amount to much more than  $1 \mu\mu$ . A deviation of the kind which we might expect from the source of errors supposed by BATES, would reveal itself, near the limit of absorption, in a displacement of the band towards this limit. Such a displacement is not at all indicated by these observations.

Let us consider what apparent displacement must have taken

place, to account for the anomalous rotations which are found in the measurements. This may be found by supposing for a moment that the rotation of the salt is normal, and by putting it equal to that of water. If for instance we start from the value  $\varphi_{\lambda_1} = 7.1$  for  $\lambda_2 = 606$ <sup>1)</sup> and we call  $\lambda_1$  the wave-length, where the band ought to have appeared with the solution, if it appeared with water at  $\lambda_2 = 519$ , then we find by a simple calculation  $\lambda_1 = 509$ , while we have observed  $\lambda_1 = 500$ . According to what has been said before a displacement of the band of  $9 \mu\mu$  cannot be apparent. Hence the validity of the results obtained before is not affected by the error supposed by BATES.

<sup>1)</sup> Comm. N<sup>o</sup>. 76 p. 4; Proc. Royal Acad. 1901/02 p. 340.

**Mathematics.** — “An equation of reality for real and imaginary plane curves with higher singularities”, By Mr. FRED. SCHUH. (Communicated by Prof. D. J. KORTEWEG.)

(Communicated in the meeting of March 19, 1904).

For a plane algebraic curve having an equation with real coefficients only and possessing no higher singularities than the four of PLÜCKER, KLEIN<sup>1)</sup> has deduced (as an extension of relations of reality found by ZEUTHEN in a  $C_4$ ) the equation

$$n + \beta' + 2\tau'' = k + \alpha' + 2\delta'' \quad . . . . . (1)$$

where

- $n$  is the order,  $k$  the class of the curve,
- $\beta'$  the number of real inflexions,
- $\alpha'$  the number of real cusps,
- $\tau''$  the number of real isolated bitangents and
- $\delta''$  the number of real isolated double points.

This equation of KLEIN can be extended to curves with *higher singularities* and it then becomes most remarkably *simpler and invariably holds good also for curves in whose equation imaginary coefficients appear*, which is not the case with the equation of KLEIN.

The equation found by me runs as follows :

$$n + \sum' v_1 = k + \sum' t_1 \quad . . . . . (2)$$

Here  $\sum' t_1$  denotes the sum of the *orders* of the singularities with *real point*,  $\sum' v_1$  the sum of the *classes* of the singularities with *real tangent*. By an *element* of the curve I understand in the following a *point* of the curve together with the *tangent* belonging to it, exclusively as forming a part of one *branch* of the curve, which can be represented by *one* single PUISEUX-development (with exponents fractional or not). The element I call a *singularity*: 1<sup>st</sup> if point or tangent or both are singular, or 2<sup>nd</sup> if point or tangent or both belong to several elements of the curve, or 3<sup>rd</sup> if the point is real and the tangent imaginary or reversely.

If through the same point more branches pass, we call the point a *manifold singular point*; this is to be regarded so many times as a singularity as there are branches passing through it. Correlative to this is a *manifold singular tangent*.

1) F. KLEIN, Eine neue Relation zwischen den Singularitäten einer algebraischen Curve. *Math. Ann.*, Bd. 10 (1876), p. 199.

With PLÜCKER<sup>1)</sup> we understand by the *order*  $t$  of a single singularity the number of the points of intersection coinciding in the (singular) point with an arbitrary line of intersection through that point. If eventually more branches pass through the singular point, we must of course count those points of intersection only, which by a slight displacement of the intersecting line are found on the branch belonging to the singularity in question. Correlative to the order is the *class*  $v$  of the singularity. This class is at the same time equal to the number of points of intersection approaching the (singular) point along the branch in question with an intersecting line passing through that point and about to coincide with the (singular) tangent.

If we regard this last quality as the definition of the class of a singularity, then the development in point coordinates with the (singular) point as origin and the (singular) tangent as axis of  $x$

becomes  $y = ax^{\frac{t+v}{t}} + \dots$ , after having given all exponents an equal denominator though as small as possible (for a small value of  $x$  gives  $t$  small roots  $y$ , on the contrary a small value of  $y$  gives  $t+v$  small roots  $x$ ). If farthermore  $X$  and  $Y$  are the line coordinates of the straight line  $y + Xx + Y = 0$ , then the development

in line coordinates becomes  $Y = AX^{\frac{t+v}{v}} + \dots$ , from which ensues the correlativeness of  $t$  and  $v$ . At the same time it is evident from this that order and class of a singularity can be read immediately from the corresponding development, from those in point coordinates as well as from those in line coordinates.

In (2)  $\Sigma' t_1$  denotes a summation with respect to the singularities with real point,  $\Sigma' v_1$  to the singularities with real tangent, where a manifold singularity must be taken into consideration as many times as it possesses single singularities. Here not only the higher and PLÜCKER-singularities must be counted, but also those elements of the curve, the counting of which has an influence on the equation (2); thus also those elements ( $t = v = 1$ ) of which the point is real and the tangent imaginary or reversely. It is clearly indifferent

<sup>1)</sup> J. PLÜCKER. Theorie der algebraischen Curven. Bonn, A. Marcus, 1839, p. 205.

<sup>2)</sup> O. STOLZ. Ueber die singulären Punkte der algebraischen Functionen und Curven. *Math. Ann.*, Bd. 8 (1875), p. 415 (spec. p. 441—442).

H. G. ZEUTHEN. Note sur les singularités des courbes planes. *Math. Ann.* Bd. 10, p. 210 (spec. p. 211—212).

H. J. STEPHEN SMITH. On the Higher Singularities of Plane Curves. *Proc. London Math. Soc.*, Vol. 6 (1874—75), p. 153 (spec. p. 163—164).

whether we do or do not include entirely real or entirely imaginary non-singular elements among the  $\Sigma'$ -signs.

*The equation (2) holds good for curves with imaginary equation as well as for curves with real equation.*

Now follow the chief points of the deduction of the equation discussed. This will be given more minutely in my dissertation<sup>1)</sup> still to appear.

To this end we shall treat in § 1, 2 and 3 the relation (2) for curves with real equation, taking that of KLEIN as our starting point. In § 4 we shall indicate it for curves with imaginary equation too, and in § 5 we shall transform it to other forms.

§ 1. *Curves with real equation and with no other manifold singularities than double points and bitangents.*

For the present we shall take a one-sided point of view where a curve is regarded as a locus of points.

If the curve has higher unifold singularities we *dissolve* them. This means that we bring about such a small *real* modification in the equation in point coordinates with preservation of the order, that the higher singularities disappear without PLÜCKER-point-singularities (cusps and double points) taking their place (but of course inflexions and bitangents). After this dissolution, where we assumed the PLÜCKER-singularities already present to be remaining, we apply the equation of KLEIN.

To this end we must consider how many isolated bitangents and how many real inflexions appear in the dissolution of a higher singularity. In two ways isolated bitangents can be formed, namely 1<sup>st</sup> in the dissolution of a *real singularity*, i. e. a singularity whose corresponding singular branch is real, 2<sup>nd</sup> in the dissolution of two conjugate imaginary singularities; here point as well as tangent must be imaginary, as otherwise we should be treating a manifold singularity, which we exclude from this paragraph. Of course real inflexions can arise only from the dissolution of *real* singularities.

By dissolving the singularity the class of the curve undergoes an increase  $d$ . Here  $d$  represents *the reduction of class* of the singularity (called by SMITH, l.c., p. 155 the *discriminantal index*) i.e. the

<sup>1)</sup> Over den invloed van hoogere singulariteiten op aanrakingsproblemen van vlakke algebraïsche krommen. (On the influence of higher singularities on problems of contact of plane algebraic curves.)

multiplicity of the singular point as point of intersection of the curve with the first polar of an arbitrary point.

INFLUENCE OF A REAL SINGULARITY. Suppose when dissolving a real higher singularity with a reduction of class  $d_1$ , we arrive at  $\beta'_1$  real inflexions and  $\tau''_1$  isolated bitangents. The class then becomes  $k + d$  so that ensues from the equation of KLEIN, if for simplicity's sake we think the curve to possess but *one* higher singularity :

$$n + \beta' + 2\tau'' + \beta'_1 + 2\tau''_1 = k + d_1 + \alpha' + 2\sigma''.$$

What the value is of  $\beta'_1$  and of  $\tau''_1$  separately, depends upon the manner of dissolution. If however we apply the above equation to curves formed in different manners of dissolution, we find that  $\beta'_1 + 2\tau''_1$  has always the same value, called by me the *reduction of reality* of the singularity. In my dissertation I shall deduce out of a definite manner of dissolution for that reduction of reality the value  $d_1 + v_1 - t_1$ , which causes the latter equation to become

$$n + \beta' + 2\tau'' + v_1 = k + \alpha' + 2\sigma'' + t_1 \quad (3)$$

INFLUENCE OF TWO CONJUGATE IMAGINARY SINGULARITIES. As we excluded

1) This equation agrees with the *index of reality* given by A. BRILL (Ueber Singularitäten ebener algebraischer Curven und eine neue Curvenspecies. *Math. Ann.*, Bd. 16 (1880), p. 348, spec. p. 391) based upon the decomposition of the higher singularity in PLÜCKER-singularities. A. CAYLEY (On the Higher Singularities of a Plane Curve. *Quart. Journ. of Math.*, Vol. 7 (1866), p. 212, *Collected Math. papers*, Vol. 5, p. 520) has namely shown, although in a not entirely satisfactory way, that the PLÜCKER-equations as well as the equation of deficiency keep holding good for curves with higher singularities, if we regard such a singularity as equivalent to  $\alpha^*$  cusps,  $\beta^*$  inflexions,  $\delta^*$  double points and  $\tau^*$  bitangents. For  $\alpha^*$  and  $\beta^*$  CAYLEY gives

$$\alpha^* = t - 1 \quad , \quad \beta^* = v - 1 \quad , \quad . . . . . (4)$$

and he indicates how  $\delta^*$  and  $\tau^*$  can be deduced from the PUISEUX-developments in point and line coordinates.

Later on fuller proofs for the results of CAYLEY have been furnished, among which that of STEPHEN SMITH excels for its simplicity and rigorousness (l. c., p. 153—162), based upon the line of thoughts of CAYLEY. For the CAYLEY-numbers of equivalence SMITH introduces (l. c., p. 161) the names *cuspidal index*, *inflexional index*, *nodal index* and *bitangential index* and among them he finds a simple relation (l. c., p. 166).

BRILL has shown that this CAYLEY-equivalence does not only completely satisfy the PLÜCKER-equations and the equation of deficiency, but that it is possible to deform the curve retaining order, class and deficiency in such a way that the higher singularities are decomposed into the equivalent ones of PLÜCKER. BRILL calls this operation a *deformation* of the singularity (i. e. p. 361). Already CAYLEY (On the Cusp of the second kind or Nodecusp. *Quart. Journ. of Math.*, Vol. 6 (1864), p. 74, *Collected Math. papers*, Vol. 5, p. 265) gives for the case of a ramphoid cusp an example of a such like deformation although he does not emphatically draw the attention to the fact that class and deficiency remain unaltered.

In an elegant way BRILL indicates further algebraically, that for every real defor-

from this paragraph the manifold higher singularities, point and tangent of conjugate imaginary singularities must both be imaginary. If we decompose those singularities into the equivalent ones of PLÜCKER in the manner indicated by BRILL (see note), thus without changing order and class of the curve, then of those PLÜCKER-singularities point as well as tangent are imaginary, as was also the case with the original singularities. So no PLÜCKER-singularities are formed, which appear in the equation of KLEIN, so that that equation invariably holds good for a curve, possessing only higher singularities of which point and tangent are both imaginary.

Comprising the results of this paragraph, we thus find for a curve without manifold higher singularities the equation

$$u + \beta' + 2\tau'' + \Sigma'v_1 = k + \alpha' + 2\delta'' + \Sigma't_1, \dots \quad (5)$$

where the summations must be extended only to the *real higher singularities*.

## § 2. *Curves with real equation and with manifold higher singularities.*

If the curve has manifold higher singularities, we can imagine that these are driven asunder in the separate singularities in such a way by a slight *real* modification in the equation of the curve retaining order and class of the curve, that its singular points and tangents all differ, but without the nature of the separate singularities having undergone a change. This operation which I shall explain more minutely in my dissertation for the case of one manifold singularity only, I call the *dispersion* of the manifold singularity <sup>2)</sup>.

mation of a higher singularity  $\alpha^{*'} - \beta^{*'} + 2(\delta^{*''} - \tau^{*''})$  retains the same value, which he calls the *index of reality* of that singularity. Here  $\alpha^{*'}$ ,  $\beta^{*'}$ ,  $\delta^{*''}$ ,  $\tau^{*''}$  represent the numbers of the real cusps and inflexions and of the isolated double points and bitangents, generated at the deformation. How large those numbers are separately depends on the manner of deformation.

This however is not a new result, but an immediate consequence of the equation of KLEIN if after various deformations we apply it to a curve possessing at first but *one* higher singularity.

BRILL (l. c. p. 391) says he intends to point out elsewhere that the index of reality of a singularity (however, this must run: of a *real* singularity) amounts to  $\alpha^{*'} - \beta^{*'}$ , so according to (4) to  $t - v$ . In connection with

$$u + \beta' + 2\tau'' + \beta^{*'} + 2\tau^{*''} = k + \alpha' + 2\delta'' + \alpha^{*'} + 2\delta^{*''}$$

the equation (3) follows immediately from it. However I am not aware where BRILL gives the promised proof.

<sup>2)</sup> So here we leave the one-sided point of view of the beginning of § 1.

By this dispersion however new isolated double points and isolated bitangents are formed, but the higher manifold singularities disappear, so that the equation (5) is applicable, provided among  $\delta''$  and  $\tau''$  the newly generated isolated double points and bitangents are counted. These however can be formed only as points of intersection and common tangents of two conjugate imaginary branches.

Here are three cases to be distinguished with respect to the reality of the two points and tangents of the manifold singularity consisting of two conjugate imaginary branches. The case already discussed, that the points and the tangents are both imaginary, does not give rise to a manifold singularity, so it does not come into consideration now.

POINTS OF CONTACT REAL, TANGENTS IMAGINARY. From both branches being *conjugate* imaginary ensues that the points of contact coincide, but that the tangents differ. If the order of each of the singularities is  $t$ , then both branches intersect each other in  $t^2$  coinciding points, which after the dispersion of the singular points cause  $t^2$  double points to be generated. If that dispersion takes place, as we keep assuming, in such a way that the equation of the curve remains real, then the singular points become conjugate imaginary, whilst the singular tangents remain imaginary. So after the dispersion we get singularities which have no influence on the equation of KLEIN. However we have got another  $t^2$  double points of which  $t(t-1)$  are imaginary and  $t$  are isolated. The latter is easy to understand by causing the  $t$  coinciding tangents of each of the singularities to diverge a little before the dispersion, by which each of the two singularities changes into a common  $t$ -fold point with separated but slightly differing imaginary tangents. The  $t$  tangents originating from the one singularity are conjugate to those of the other. With the dispersion the  $t$  pair of conjugate imaginary tangents give  $t$  isolated points, whilst the remaining double points become imaginary.

After the dispersion of the singular points by which the number of isolated points has become  $\delta'' + t$  and the number of isolated bitangents has remained invariable, we find by applying the equation (5)

$$n + \beta' + 2\tau'' + \Sigma' v_1 = k + \alpha' + 2(\delta'' + t) + \Sigma' t_1.$$

For this again we may write :

$$n + \beta' + 2\tau'' + \Sigma' v_1 = k + \alpha' + 2\delta'' + \Sigma' t_1, \quad \dots \quad (5)$$

if we but extend  $\Sigma' t_1$  to those higher singularities of which the point is real but the tangent imaginary.

POINTS OF CONTACT IMAGINARY, TANGENTS REAL. This case is quite correlative to the preceding. Now the points of contact are different, whilst the tangents coincide. Out of this common tangent is formed

by the dispersion of the singular tangents  $v^2$  new bitangents, of which  $v$  are isolated. So for this case too the equation (5) holds good if we but extend  $\Sigma'v_1$  to those higher singularities of which the point is imaginary but the tangent is real.

POINTS OF CONTACT AND TANGENTS BOTH REAL. Now point and tangent of both imaginary singularities coincide. So the two branches touch each other. This may be an ordinary contact or a higher one, as the PUISEUX-developments of both singularities correspond in the first terms (which are then real); the unequal terms are conjugate imaginary.

If  $t$  and  $v$  denote order and class of each of the singularities and  $c$  a number which need not be known more closely, the numbers  $D$  and  $T$  respectively of the coinciding points of intersection and of the coinciding common tangents of both branches amount to

$$\left. \begin{aligned} D &= t^2 + c, \\ T &= v^2 + c. \end{aligned} \right\} \dots \dots \dots (6)$$

This ensues from a relation which always exists for two singular branches touching each other between the numbers  $D$  and  $T$ , namely

$$T - D = (\beta_1^* + 1)(\beta_2^* + 1) - (\alpha_1^* + 1)(\alpha_2^* + 1),$$

where  $\beta_1^*$  and  $\beta_2^*$  denote the inflectional indices,  $\alpha_1^*$  and  $\alpha_2^*$  the cuspidal indices of both singularities<sup>1)</sup>. This relation was first deduced by STEPHEN SMITH (l.c., p. 167). If according to (4)<sup>1)</sup> we express the indices in order and class of the singularities, we find

$$T - D = v_1 v_2 - t_1 t_2,$$

or, as in our case  $t_1 = t_2 = t$  and  $v_1 = v_2 = v$ ,

$$T - D = v^2 - t^2,$$

from which ensue the two equations (6).

If therefore we disperse both singularities in such a way that the singular points and tangents begin to differ, this causes point and tangent to become imaginary, whilst  $D$  new double points and  $T$  new bitangents appear. If among these are  $D'$  isolated double points and  $T''$  isolated bitangents, then

$$\left. \begin{aligned} D'' &= t + c', \\ T'' &= v + c'. \end{aligned} \right\} \dots \dots \dots (7)$$

which I shall prove more minutely in my dissertation.

By the dispersion of the singularities the numbers of the isolated double points and bitangents have become  $d'' + t + c'$  resp.  $\tau'' + v + c'$ . So the equation (5) gives

$$u + \beta' + 2(\tau'' + v + c') + \Sigma'v_1 = k + \alpha' + 2(d'' + t + c') + \Sigma't_1.$$

So before that dispersion

<sup>1)</sup> See note p. 767-768.

$$n + \beta' + 2 \tau'' + \Sigma' v_1 = k + \alpha' + 2 \sigma'' + \Sigma' t'', \dots (5)$$

where the two summations must also be extended to the imaginary singularities with real points and tangents.

§ 3. Proof of equation (2) for a curve with real equation.

The considerations of the two preceding paragraphs all lead up to the equation (5) thus holding good for every curve with real equation and with higher singularities. The summations must be extended only to the *higher* singularities, namely  $\Sigma' t_1$  to those with real points,  $\Sigma' v_1$  to those with real tangents.

The equation (5) can be considerably simplified by including also the PLÜCKER-singularities among the  $\Sigma'$ -signs.

INFLEXION. For an inflexion we have  $t = 1, v = 2$ . If we omit  $\beta'$  but extend  $\Sigma' t_1$  and  $\Sigma' v_1$  to the real inflexions then in (5) due consideration is taken of the presence of those inflexions.

CUSP. For this  $t = 2, v = 1$ , so that for the cusps the same holds good as for the inflexions.

ISOLATED POINT. An isolated point is formed by two conjugate imaginary elements, of which the points are real, thus coinciding, the tangents imaginary, thus differing. For each of those elements  $t = v = 1$ . If we extend the summations to the isolated points, this has no influence on  $\Sigma' v_1$  (the tangents being imaginary), whilst on the contrary  $\Sigma' t_1$  increases with  $2\sigma''$ . If now in (5) we omit the term  $2\sigma''$ , but extend  $\Sigma' t_1$  to the isolated points, the equation remains true.

ISOLATED BITANGENT. This is formed by two elements ( $t = v = 1$ ) with real tangents and imaginary points of contact. For this holds good the correlative of what was observed for an isolated point.

So if the summations are extended also to the PLÜCKER-singularities the equation (5) becomes

$$n + \Sigma' v_1 = k + \Sigma' t_1, \dots (2)$$

where, if one pleases, every other element of the curve may be included among the  $\Sigma'$ -signs.

§ 4. Proof of equation (2) for a curve with imaginary equation.

To prove the relation (2) for a curve with imaginary equation, we write it in the form:

$$J \equiv k - n + \Sigma' t_1 - \Sigma' v_1 = 0.$$

So we must show, that also for a curve with imaginary equation  $J$  has the value zero. Let  $\varphi + i\psi = 0$  be the equation of that



$$3(k - u) = \Sigma v_1 - \Sigma t_1 \dots \dots \dots (9)$$

The equation of reality (2), can thus be written in the following form:

$$\Sigma t_1 - \Sigma v_1 = 3(\Sigma' t_1 - \Sigma' v_1) \dots \dots \dots (10)$$

If furthermore  $\Sigma'' t_1$  indicates a summation over the *imaginary points*,  $\Sigma'' v_1$  over the *imaginary tangents*, then  $\Sigma t_1 = \Sigma' t_1 + \Sigma'' t_1$ , etc. so that (10) becomes

$$\Sigma'' t_1 - \Sigma'' v_1 = 2(\Sigma' t_1 - \Sigma' v_1) \dots \dots \dots (11)$$

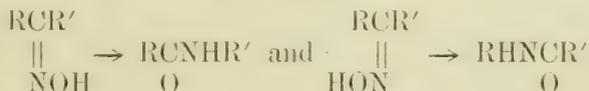
The equations (2), (9) and (10) are of course but different forms for the same relation of reality.

*Sneck*, March 1904.

**Chemistry.** — Professor LOBRY DE BRUYN presents communication N° 7 on intramolecular rearrangements: C. A. LOBRY DE BRUYN and C. H. SLUITER. "*The BECKMANN-rearrangement; transformation of acetophenoxime into acetanilide and its velocity.*"

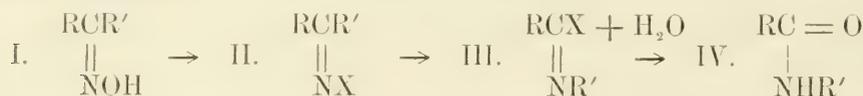
(Communicated in the meeting of February 27, 1904).

Among the many intramolecular rearrangements known in organic chemistry, the one associated with the name of BECKMANN belongs to one of the most important series on account of the extent of its region and its scientific significance. As is well known, it consists in the transformation of the oximes, under the influence of a certain number of reagents, into the isomeric acid amides, for instance:  $R_2CNOH \rightarrow RCONHR$ . Its extent is obvious if we remember that all ketones and aldehydes are capable of yielding oximes and that a large number of these, particularly of the ketoximes, can undergo the rearrangement. Its scientific importance is chiefly due to the fact that its application to the stereoisomeric ketoximes has been the means of determining the configuration of those stereoisomers, in this manner:

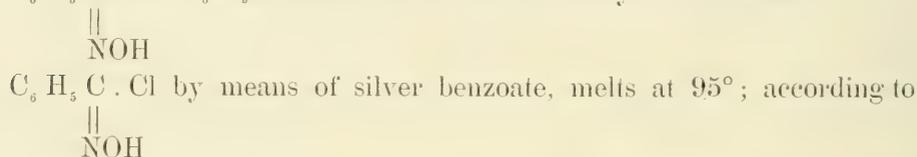


The rearrangement generally takes place under the influence of different reagents such as sulphuric acid, hydrochloric acid, phosphorus pentachloride and -oxide, acylchlorides, acetic acid with its anhydride and HCl, zincchloride, alkalis. As these substances are always applied in relatively large quantities, it is thought most probable, that the actual rearrangement nearly always relates to inter-

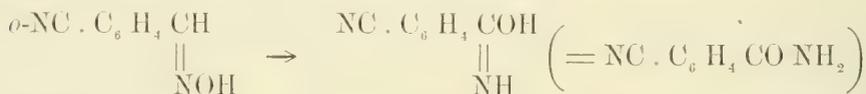
mediate products, additive compounds or derivatives of the oximes, which occasionally have been separated <sup>1)</sup>. These intermediate products then contain a negative group (or the group OK) attached to the nitrogen which changes place with the C-combined alkyl- or aryl-group. On subsequent treatment with water the amide is generated. We then have :



That hydroxyl itself can assume the function of the group X which changes place with R' is shown by the interesting observations of WERNER and BUSS <sup>2)</sup>, WERNER and SKIBA <sup>3)</sup>, POSNER <sup>4)</sup> and AUWERS and CZERNY <sup>5)</sup>, who have noticed some cases of the BECKMANN-rearrangement in the absence of any reagent. Dibenzhydroximic acid  $\text{C}_6\text{H}_5\text{COCO}\text{C}_6\text{H}_5$  obtained from chlorobenzhydroximic acid



WERNER and BUSS it changes after some days spontaneously into its isomer  $\text{C}_6\text{H}_5\text{CO} \cdot \text{NHO}\text{CO}\text{C}_6\text{H}_5$  m.p. 161°; on heating this takes place more rapidly. POSNER observed that *o*-cyanobenzaldoxime changes into its isomer when simply heated above its melting point; it first melts at 175°, then solidifies and finally melts again at 203°. Here we consequently have the direct conversion :



Finally, AUWERS and CZERNY have found that *o*-oxy-*m*-methylbenzophenonoxime:  $\text{HO} \cdot \text{H}_3\text{C}\text{C}_6\text{H}_3\text{C} \cdot \text{C}_6\text{H}_5$  partly undergoes the



BECKMANN-rearrangement when submitted to distillation.

These observations from WERNER and his pupils, of POSNER and of AUWERS and CZERNY are of fundamental importance for the under-

<sup>1)</sup> BECKMANN for instance (Ber. 19. 988) obtained  $\text{C}_6\text{H}_5\text{CCl} : \text{NC}_6\text{H}_5$  from  $(\text{C}_6\text{H}_5)_2\text{C} : \text{NOH}$  and  $\text{PCl}_5$ . It is very probable that  $(\text{C}_6\text{H}_4)_2\text{C} : \text{NCl}$  is formed first as an intermediate product.

<sup>2)</sup> Ber. 27, 2198 (1894).

<sup>3)</sup> Ber. 32, 1654 (1899).

<sup>4)</sup> Ber. 30, 1693 (1897).

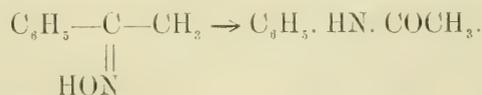
<sup>5)</sup> Ber. 31, 2692 (1898).

standing of the mechanism of the BECKMANN-rearrangement. They prove that this important transformation is most decidedly a real intramolecular rearrangement, which may occur in some cases with the oxime, but in the majority of cases with derivatives in which, instead of the OH-group, another negative group or a halogen has been attached to the nitrogen. In that case the change from II into III represents the actual rearrangement.

ATWERS and CZERNY have already pointed out that the above rearrangement caused by distillation deserves the closest attention. They are of opinion that this observation leads to the view that the BECKMANN-rearrangement is a catalytical process which is in accord with BECKMANN's own ideas. But is it permissible to speak of a catalytic process when the catalyzer is wanting? And do not ATWERS and CZERNY withdraw their own statement when they say that "es sich vielmehr handelt um die directe Ueberführung eines weniger stabilen System in ein stabileres?"

The BECKMANN-rearrangement has not, up to the present, been subjected to a dynamical investigation. Such a study is not rendered less desirable or less important by the fact that, as a rule, the rearrangement of the intermediate product and not that of the oximes themselves will be investigated.

The oxime which has been studied in the first place is acetophenoxime of which only one form is known and which quantitatively passes into acetanilide. Its configuration is therefore:



The rearrangement, which BECKMANN found to take place under the influence of concentrated sulphuric acid was studied in the first place. Before starting it was necessary to work out an analytical method allowing the quantitative determination of the resulting anilid in the presence of the unchanged oxime. After several preliminary experiments it was found that the anilide formed on adding water was completely hydrolyzed by boiling for a few hours and that the acetic acid could then be distilled off and titrated; the excess of oxime did not interfere. We have in consequence determined the velocity with which the anilide was formed. In carrying out the experiments 2.5 grams of the oxime were dissolved in 50 or 100 cc. of sulphuric acid, previously heated to the temperature at which the experiment was made (60° or 65°) and at definite periods a certain quantity was pipetted off from the bottle (which was placed in a thermostat) and analysed.

The reaction proved to be one of the first order, the velocity constant did not change with the concentration; so it is a monomolecular one. At 65°, for instance  $k = 0.0019$  for a solution of 2.5 grams of the oxime in 50 as well as in 100 cc. of 93.6% sulphuric acid (time in minutes; transformation of  $\frac{1}{2}$  of the oxime after 160 minutes).

The transformation velocity increases with the concentration of the acid as shown from the following table:

Temp. 60°. Concentration H <sub>2</sub> SO <sub>4</sub> .	Velocity- constant.	Time of $\frac{1}{2}$ transformation.
93.6	0,0011	275 min.
94.6	13	232
97.2	38	75
98.7	70	43

At 65°, a 86.5% sulphuric acid gave a constant of 0.0006 (time of  $\frac{1}{2}$  transformation = 501 minutes). When using 99.2% acid at 60°, practically all the oxime had been converted after 15 minutes.

The influence of the temperature is apparent from the following figures:

at 60°, 93.6% H<sub>2</sub>SO<sub>4</sub>,  $k = 0,0011$ ; 94.6% H<sub>2</sub>SO<sub>4</sub>,  $k = 0,0013$   
 65°, „ „ „ „ = 0,0019 „ „ „ = 0,0021

The temperature-coefficient for 10° is therefore about 3.

A solution of SO<sub>3</sub> in chloroform did not appear to cause any transformation of the oxime.

The results of this research therefore confirm the view that in the BECKMANN-transformation we are dealing with a real intramolecular rearrangement. Even if the application of sulphuric acid should cause the formation of an intermediate compound (which has not yet been positively proved, but which is very probable<sup>1)</sup>) our experiments show that this formation (or the conversion I into II) takes place with immeasurably great velocity. The very perceptible development of heat which occurs on mixing the oxime with the concentrated sulphuric acids also points to this fact.

*Addendum.* Of late years, STIEGLITZ and his coworkers (Amer. Chem. J. 1896—1903) have been engaged in the study of the BECKMANN-rearrangement. In my opinion STIEGLITZ's ideas cannot be accepted in their entirety. Recently this chemist has given a summary of his conclusions in a separate article "on the BECKMANN-rearrange-

<sup>1)</sup> If to an ethereal solution of the oxime is added a solution of sulphuric acid in ether, a precipitate is obtained the nature of which will be investigated.

ment" (Amer. Chem. J. 7, **29**, 49 (1903)). He then arrives at the following views.

The analogy of the HOFMANN-transformation of the amides into amines with the BECKMANN-rearrangement (an analogy first pointed out by HOOGEWERFF and VAN DORP (Rec. **6**, 373, **8**, 173 etc.)) and the fact that the acid azides of CURTIUS are converted with elimination of nitrogen into the same isocyanates which occur as intermediate products in the HOFMANN-transformation, induces STIEGLITZ to attempt to explain these reactions from a same point of view. He believes that in the three above transformations there must be formed intermediate molecule-residues containing univalent nitrogen; with the azides for instance  $\text{CH}_3\text{CO.N.N}_2 \rightarrow \text{CH}_3\text{CO.N} + \text{N}_2$ ; with the bromoamides for instance,  $\text{CH}_3\text{CONHBr} \rightarrow \text{CH}_3\text{CO.N} + \text{HBr}$ . These molecule-residues are then supposed to be converted straight into the isocyanate:  $\text{CH}_3\text{—CO.N} \rightarrow \text{CONCH}_3$ . In order to arrive, in the transformation of oximes into amides, at such molecules with univalent N-atoms, STIEGLITZ assumes that first of all HCl is attached to the oxime owing for instance to the action of  $\text{PCl}_5$ ,  $\text{R}_2\text{C}=\text{NOH} + \text{HCl} \rightarrow \text{R}_2\text{CCl—NHOH}$ ; this additive compound under the influence of  $\text{PCl}_5$  then loses one mol., of water and gives  $\text{R}_2\text{CCl—N}$  which molecule-residue is then supposed to be converted into  $\text{RCCl}=\text{NR}$ , which on treatment with water yields the amide.

Now, first of all it is difficult to see where the HCl, which gets attached to the oxime, is to come from; it is of course known that some oximes yield with  $\text{PCl}_5$  compounds such as  $\text{R}_2\text{CClN}$  with formation of HCl, but this is not the formation which STIEGLITZ had in mind. We also fail to see how sulphuric acid, acting as dehydrating reagent will, in the rearrangement, cause a mol. of water to be first attached and then to be again eliminated; neither do we understand how the transformation under the influence of, say,  $\text{P}_2\text{O}_5$  or  $\text{ZnCl}_2$  can be reconciled with the ideas of STIEGLITZ. Finally, STIEGLITZ himself admits of his own theory that "it does not agree so well with the more obscure relations of the theory of stereoisomerism of ketoximes and their influence on the rearrangement of these isomers. It is hoped that future work will remove this difficulty". (Am. Ch. J. 7, **29**, 67). The difficulty is this, that STIEGLITZ theory utterly ignores a fact of fundamental importance, namely the formation of two different amides from the stereoisomeric ketoximes; these according to STIEGLITZ ought to lead to the same intermediate product from which the same amide only could be formed. And finally the transformations of an oxime into the isomeric amide without any reagent whatever, as observed by WERNER and his

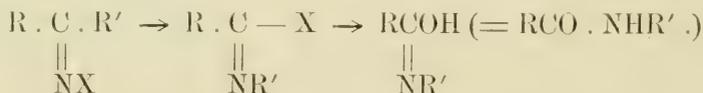
coworkers, by POSSNER and by AUWERS and CZERNY are directly opposed to his representations.

In his last theoretical paper, STIEGLITZ attributes the transformation of some more hydroxylamino-derivates to the intermediary formation of molecule-residues with univalent nitrogen; he includes all these under the name of "BECKMANN-arrangement".

I think, I have shown that this classification is not permissible. If it were so, the HOFMANN-transformation might claim priority over the "BECKMANN-arrangement", which is of more recent date.

In order to avoid confusion I think it absolutely necessary to let each of the said transformations retain its own name and to treat them as separate reactions. In the CURTIUS-transformation  $\text{CH}_3\text{CON} \cdot \text{N}_2 \rightarrow \text{CONCH}_3 + \text{N}_2$ , the assumption of the intermediary occurrence of a molecule residue  $\text{CH}_3\text{CO} \cdot \text{N}$  is permissible; in the HOFMANN-reaction  $\text{CH}_3\text{CONHBr} \rightarrow \text{CONCH}_3 + \text{HBr}$  such is possible but not necessary,  $\text{Br} \cdot \text{C} - \text{OK}$

$\begin{array}{c} \parallel \\ \text{NCH}_3 \end{array}$  may also have been formed as an intermediate product (HANTZSCH); finally we may admit in the BECKMANN rearrangement.



a same mechanism as in the HOFMANN-transformation, but according to my opinion, not the presence of a molecule-residue with univalent nitrogen.

The physico-chemical investigation of the BECKMANN-rearrangement is being continued.

LOBRY DE BRUYN.

Amsterdam, February 1904.

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1) X = Cl, Br, OH or  $\text{SO}_2\text{H}$  [respectively  $\text{H}_2\text{SO}_4$ ],  $\text{OCOCH}_3$ .

**Chemistry.** — Prof. C. A. LOBRY DE BRUYN presents communication N<sup>o</sup>. 8 on intramolecular rearrangements: C. L. JUNGHUS. “*The mutual transformation of the two<sup>1)</sup> stereoisomeric pentacetates of d-glucose.*”

(Communicated in the meeting of March 19, 1904).

1. It is well known that the esterification of alcohols by means of acetic anhydride is accelerated in a high degree by the presence of catalyzers and this of course also applies to the sugars. But it is a remarkable fact that in the case of these polyhydric alcohols we arrive at various isomeric pentacetates according to the nature of the catalyzer. The investigations of FRANCHIMONT<sup>2)</sup> and of HERZFELD<sup>3)</sup> have shown that, when dry sodiumacetate is used as catalyzer, we obtain a product melting at 134° ( $\beta$ ), whilst according to ERWIG and KÖNIGS<sup>4)</sup> treatment with ZnCl<sub>2</sub> yields a product melting at 112° ( $\alpha$ ). After FRANCHIMONT had proved that these two compounds were in reality isomeric<sup>5)</sup> [the first was formerly thought to be a diglucose-octacetate] this chemist supported the view that they may be best represented as derived from the so-called oxide-form of glucose<sup>6)</sup>. The two pentacetates will then be stereoisomers as the oxide-form of glucose, which contains one asymmetric carbon atom more than the aldehyde-form, must give rise to two isomers.

As in the case of the two methylglucosides<sup>7)</sup> we arrive, on applying TOLLENS' glucose formula, at the following constitution of the pentacetates:



The existence of two isomers is explained by the fact that the terminal C-atom on the left appears as a new asymmetric atom.

2. It was known that the  $\beta$ -isomer formed by sodiumacetate is

<sup>1)</sup> A few years ago, TAXRET described a third isomeric glucosepentacetate m.p. 86° (Bull. **13**. 261 (1895). My investigation has led me to the conclusion that this isomer does not exist but is a mixture of the other two.

<sup>2)</sup> Ber. **12**. 1940.

<sup>3)</sup> Ber. **13**. 265.

<sup>4)</sup> Ber. **22**. 1464.

<sup>5)</sup> Recueil. **11**. 106 (1892) Recueil. **12**. 310.

<sup>6)</sup> These Proc. June 24 1893.

<sup>7)</sup> E. FISCHER B. **26**. 2400 (1893).

<sup>8)</sup> Ac = CH<sub>3</sub> — CO.

converted into the other compound by boiling its solution in acetic anhydride for a short time with a little  $ZnCl_2$ .

I have made a closer study of this transformation; it is caused by an intramolecular migration at the terminal asymmetric carbon atom. One might feel disposed to explain the transformation in an acetic anhydride solution by an addition and subsequent elimination of a molecule of the solvent, such as FISCHER supposed to happen in the mutual transformation of the two isomeric methylglucosides<sup>1)</sup>. This view, however, becomes untenable as the transformation can also take place without the presence of acetic anhydride. Then LOBRY DE BRUYX, by simply melting the  $\beta$ -isomer m.p.  $134^\circ$  with dry  $ZnCl_2$ , at once obtained the other compound m.p.  $112^\circ$ . I also succeeded in causing the same transformation in a chloroform solution containing  $SO_3$ . On shaking chloroform with fuming sulphuric acid, a portion of the  $SO_3$  passes into the chloroform. This solution has been found to accelerate many reactions by catalytical action. A solution of the  $\beta$ -pentacetate in  $CHCl_3$  which contained 18.8 milligrs. of  $SO_3$  per cc. at first rotated but slightly towards the right; after a short time its rotatory power had increased. The  $SO_3$  was now removed by means of dilute alkali and the chloroform distilled off. The residue was recrystallised from alcohol and in this way the pure  $\alpha$ -isomer m.p.  $112^\circ$  was obtained.

3. As in the case of the two methylglucosides, the final condition in the transformation between the two stereoisomers is here also an equilibrium; the limit however is situated close to the form melting at  $112^\circ$ . A solution prepared by dissolving 5 grams of  $\beta$ -pentacetate in 100 cc. acetic anhydride (containing 2 grams of zincchloride) showed an initial rotation of  $+1^\circ$  (polariscope SCHMIDT and HAENSCH; 10 cm. tube). On keeping this solution at  $35^\circ$ , the rotation increased with measurable velocity and finally arrived at  $+14^\circ.5$ . In the case of a quite similar solution of the  $\alpha$ -isomer, having an initial rotation of  $+16^\circ.3$  the final rotation was also  $+14^\circ.5$ . From this we calculate that in the condition of equilibrium there exists 88% of the  $\alpha$  and 12% of the  $\beta$ -compound. The former could in fact be isolated in a pure condition; in addition also some crystals which melted at  $95-98^\circ$  and contained both isomers.

4. By determining at definite times the said changes in the rotation the velocity of the mutual transformation could be measured.

It conformed with the formula for the bimolecular reversible

<sup>1)</sup> Compare my communication, these Proc. June 27, 1903.

transformation ; for  $\frac{1}{t} \log. \frac{a_x - a_0}{a_x - a}$ ) was found a constant value which was the same in the case of either isomer.

This average value representing the sum of the velocity constants of the two contrary reactions is 0.0095 (the time expressed in hours and using ordinary logarithms) at 35° and a concentration of 2% zincchloride. At 45° and 2% ZnCl<sub>2</sub>, the average constant was 0.028. The temperature coefficient of the transformation for every 10° is, therefore, 3.01. Further determinations were also made with 1% solutions of zincchloride at 45° and the constant was found to be 0.0135. This seems therefore to be proportionate to the concentration of the catalyzer.

5. Besides these two isomers, TANRET (Bull. 1895, **13**, 261) imagined to have found a third glucose-pentacetate.

On treating glucose with acetic anhydride and a little zincchloride and recrystallising the product from alcohol, he obtained from the mother-liquor crystals with  $[\alpha]_D = +59^\circ$  at 62°. This substance had no sharply defined melting point situated below the melting points of the above isomers. As he could not effect a further separation of these crystals by recrystallisation, he took it to be a third modification with a melting point of about 86°, but still occluding a small quantity of the other two, which it was difficult to get rid off. It is however obvious that this so-called third modification is only a mixture of the other two, which is deposited from an alcoholic solution saturated with both compounds. The following facts are in favour of this view.

1<sup>st</sup>. If it were a third isomer, it might be got perfectly free from the others by recrystallisation and present a definite melting point.

2<sup>nd</sup>. If we make a mixture of the isomers melting at 134° and 112° so that  $[\alpha]_D = 60^\circ$  the product will show the same melting-traject as that of TANRET<sup>2)</sup>, namely 91—94°.

3<sup>rd</sup>. A solution saturated with both isomers, and a saturated solution of TANRET's product appear to contain the same amount of pentacetate. I have used 50% alcohol as solvent. On shaking at 25° with an excess of the two pure isomers a solution was obtained containing 3.08—3.10 % of pentacetate; TANRET's product similarly treated gave a solution containing 3.13—3.14 %.

1)  $\alpha_x$  is the rotation in the condition of equilibrium,  $\alpha_0$  the initial rotation,  $\alpha$  the same at a stated period.

2) Mr. TANRET had the kindness to forward a specimen of his preparation to Prof. LOBRY DE BRUYN. With this sample the experiments have been made.

It is therefore not a matter of doubt that a third isomer does not exist but that it is a mixture of the other two <sup>1)</sup>.

The two stereoisomeric methylglucosides may be converted into the corresponding pentacetates and conversely, the latter into the former <sup>2)</sup>. The  $\alpha$ -glucoside corresponds with the pentacetate m.p. 112°, the  $\beta$ -glucoside with the pentacetate m.p. 134°. It is therefore as well to indicate the two pentacetates, respectively, with  $\alpha$  and  $\beta$ , as has in fact been done in the said article of BEHREND and ROTH.

6. The mutual transformation of the methylglucosides and pentacetates throws a new light on the phenomenon of the multirotation of sugars. We may accept as the most probable explanation of this phenomenon a mutual direct transformation of the two stereoisomeric modifications which must exist according to TOLLENS' glucose formula. The recently published investigations of FRANKLAND ARMSTRONG <sup>3)</sup> and of BEHREND and ROTH <sup>4)</sup> have furnished strong arguments in favour of this view.

But it must be remembered that TOLLENS' formula does not express the aldehydic properties of glucose; one is therefore inclined to assume that in a glucose solution there must occur also molecules in the aldehyde-form, or molecules which contain 1 more H<sub>2</sub>O with the group HC(OH)<sub>2</sub>. One may then also come to the conclusion that this hydrated aldehyde-form does not act as an intermediate product in the transformation between the two stereoisomeric oxide modifications <sup>5)</sup>, but that we have here a complete analogy of what takes place with the glucosides, namely that, although a direct transformation takes place between the stereoisomers, there also occurs a quantitatively insignificant, secondary reaction involving addition and elimination of the solvent. These reactions will then all be in equilibrium with each other. This point, I will also try to elucidate experimentally <sup>6)</sup>.

<sup>1)</sup> This view is also held in a quite recently published article of BEHREND and ROTH Ann. **331**, 359.

<sup>2)</sup> E. FISCHER and E. FRANKLAND ARMSTRONG. Ber. **34**, 2885.

<sup>3)</sup> Journ. Chem. Soc. **83**, 1305. 1903.

<sup>4)</sup> Ann. **331**, 359.

<sup>5)</sup> Compare MARTIN LOWRY, Journ. Chem. Soc. **75**, 212, (1899). **83**, 1314. (1903).

<sup>6)</sup> Several chemists (v. LIPPMANN, Chemie d. Zuckerarten II, 130, 990. Ber. 29, 203, Trev. Z. f. phys. Ch. **18**, 193, SIMON, C.R. **132**, 487), and myself (Ber. **28**, 3081 (1895)) have expressed the opinion that with the three  $[\alpha]_D$ 's of +106°, +53° and +22°,5 known for glucose, correspond three modifications, namely two oxide forms and one aldehyde form. After the research of Mr. JUNGIUS on the methylglucosides and the pentacetates it is practically certain that the  $[\alpha]_D$  of

The particulars of this research will be published later on elsewhere.

Amsterdam, March 1904. *Organ. Chem. Lab. of the Univ.*

**Mathematics.** — “*Regular projections of regular polytopes.*” By Prof. P. H. SCHOTTE.

We consider for this end the three regular polytopes  $A_n$ ,  $B_n$ ,  $C_n$  of the space  $S_n$  with  $n$  dimensions, which correspond respectively to the tetrahedron, the hexahedron and the octahedron of our space and setting aside the polytope  $B_n$  with its exceedingly simple properties we treat some special cases of the following two general theorems relating to  $A_n$  and  $C_n$ , of which the proof will be given elsewhere.

**Theorem I.**

“Let  $m$  represent  $\frac{1}{2}n$  or  $\frac{1}{2}(n+1)$  according to the number of dimensions  $n$  of  $S_n$  being even or odd.”

“Construe in  $m$  planes  $\alpha_1, \alpha_2 \dots \alpha_m$  congruent regular polygons with  $n+1$  [or  $2n$ ] sides; let  $q$  be the circumradius of those polygons.”

“Let us take in each of those planes a vertex of the polygon as the origin 0 and a definite sense, in which distance is counted from this origin to any other vertex along the circuit.”

“Let us place at the remaining vertices the numbers 1, 2 . . . in such a way that the number  $p$  is put in  $\alpha_k$  near the vertex which is distant from the vertex 0 in the sense assumed in  $\alpha_k$  a number  $pk$  [or  $p(2k-1)$ ] sides. In other words: let us place in  $\alpha_k$  moving round from 0 in the indicated sense the numbers 1, 2 in such a way that when continuing to a following number we skip  $k-1$  [or  $2(k-1)$ ] vertices. Here the polygon in  $\alpha_k$  can be reduced as far as the numbering goes to a regular polygon with  $\frac{n+1}{q}$  [or  $\frac{2n}{q}$ ] sides, each vertex of which bears  $q$  numbers, as soon as  $k$  and  $n+1$

53° belongs to a condition of equilibrium between the two oxide forms. The question put to me by Messrs. BEHREND and ROTH in their recent paper (Ann. 331, 359) has therefore now been answered. My former contention that glucose with  $[\alpha]_D + 106^\circ$  might crystallise from a solution in which it was not present (namely, from glucose with a  $[\alpha]_D + 53^\circ$ ) is, of course, no longer tenable. It is, as B. and R. observe, a question of the relative solubility of the two or three isomers able to be converted into each other. I had already shared this view for a considerable time. LOWRY and FR. ARMSTRONG have also expressed the opinion that it is a question of equilibrium. As stated above, Mr. JUNGIUS will try to determine the precise nature of this equilibrium.

L. D. B.

[or  $2k-1$  and  $2n$ ] have the greatest common divisor  $q$ . And for odd  $n$  the polygon is reduced in  $a_m$  in this respect to a linesegment long  $2q$  bearing at one end the even numbers  $0, 2, 4, \dots$  and at the other the odd numbers  $1, 3, 5, \dots$ ."

"Let us replace for odd  $n$  the just mentioned linesegment  $2q$  by a linesegment  $q\sqrt{2}$  bearing at its ends the same groups of numbers."

"Let us place for even  $n$  the  $m$  planes and for odd  $n$  the  $m-1$  planes and the linesegment  $q\sqrt{2}$  in such a way in the space  $S_n$  that in a common point they are rectangular to one another."

"Then the  $n+1$  [or  $2n$ ] points  $P_i$  of that space the projections of which on these  $m$  elements coincide with the vertices numbered with  $i$ , are the vertices of a regular polytope  $A_n$  with length of edges  $q\sqrt{n+1}$  [or  $C_n$  with length of edges  $q\sqrt{n}$ ]."

This double theorem where with respect to the continuous bifurcation "*this* [or *that*]" we must either always read *this* placed before the brackets or always *that* placed inside the brackets, reminds one of the decomposition of the general motion in  $S_n$  into  $m$  components for even  $n$  in  $m$  rotations, for odd  $n$  in  $m-1$  rotations and a translation. This remark is important with respect to the decomposition of the groups of anallagmatic motions belonging to  $A_n$  and  $C_n$ .

#### Theorem II.

"Let  $S_{p-1}$  and  $S_p$  be two spaces rectangular to each other in a point and let  $S_{2p-1}$  represent the space determined by them."

"Let us take in  $S_{p-1}$  a regular polytope  $A_{p-1}^{(1)}$ , in  $S_p$  a regular polytope  $C_p^{(1)}$ , having both as the index (1) indicates unity as length of edges."

"Let us number the  $p$  vertices of  $A_{p-1}$  with the pairs of numbers  $(0, p), (1, p+1), (2, p+2), \dots, (p-1, 2p-1)$  and let us assign to each of the  $2p$  vertices of  $C_p$  one of the numbers  $0, 1, 2, \dots, 2p-1$  under the condition that the  $p$  diagonals bear at the ends again the pairs of numbers  $(0, p), (1, p+1), 2(p+2), \dots, (p-1, 2p-1)$ ."

"Then the  $2p$  points  $P_i$  of  $S_{2p-1}$ , whose projections on  $S_{p-1}$  and  $S_p$  coincide with the vertices of  $A_{p-1}$  and  $C_p$  bearing the equal numbers, form the vertices of a regular polytope  $A_{2p-1}^{(\sqrt{2})}$  with length of edges  $\sqrt{2}$  which projects itself on  $S_{p-1}$  according to two coinciding  $A_{p-1}^{(1)}$  and on  $S_p$  according to a  $C_p^{(1)}$ ."

By this simple theorem we are enabled to deduce the proof of

theorem I for the polytope  $C_n$  out of the one for the polytope  $A_n$ . By repeated application we arrive at:

“A  $A_{2^q-1}^{(V^{2^{q-2}})}$  of the space  $S_{2^q-1}$  can project itself on a definite system of mutually rectangular spaces  $S_{2^q-1}, S_{2^q-2}, \dots, S_4, S_2, S_1$  respectively according to a  $C_{2^q-1}^{(V^{2^{q-3}})}$ , two coincided  $C_{2^q-2}^{(V^{2^{q-4}})}$ ,  $\dots$ ,  $2^{q-3}$  coincided  $C_4^{(V^2)}$ ,  $2^{q-2}$  coincided squares  $C_2^{(1)}$  and  $2^{q-1}$  coincided line-segments  $C_1^{(1)}$ ”.

**Mathematics.** — “On symmetric transformation of  $S_4$  in connection with  $S_r$  and  $S_l$ .” By Mr. L. E. J. BROUWER. (Communicated by Prof. D. J. KORTEWEG).

Let us for the present occupy ourselves with a particular case of symmetric transformation — the *reflection*, and let us investigate its influence on  $S_r$  and  $S_l$ . As  $S_r$  and  $S_l$  are independent of the choice of a system of axes, we make a suitable choice by selecting the  $X_4$  axis along the axis of reflection. Let us call  $\alpha_1, \alpha_2, \alpha_3, \alpha_4$  the cosines of direction of a vector before the reflection;  $\beta_1, \beta_2, \beta_3, \beta_4$  those after it; let us moreover represent  $\alpha_2' \alpha_3'' - \alpha_3' \alpha_2''$  etc. by  $\xi_{23}$  etc. and  $\beta_2' \beta_3'' - \beta_3' \beta_2''$  etc. by  $\chi_{23}$  etc. and let us call  $\lambda_{23}$  etc. the coefficients of position of a plane with sense of rotation included before the reflection and  $\mu_{23}$  etc. those after it. Then:

$$\alpha_1 = \beta_1$$

$$\alpha_2 = \beta_2$$

$$\alpha_3 = \beta_3$$

$$\alpha_4 = -\beta_4$$

$$\xi_{23} = \chi_{23}$$

$$\xi_{14} = -\chi_{14}$$

$$\xi_{31} = \chi_{31}$$

$$\xi_{24} = -\chi_{24}$$

$$\xi_{12} = \chi_{12}$$

$$\xi_{34} = -\chi_{34}$$

$$\sqrt{\xi_{23}^2 + \xi_{31}^2 + \xi_{12}^2 + \xi_{14}^2 + \xi_{24}^2 + \xi_{34}^2} = \sqrt{\chi_{23}^2 + \chi_{31}^2 + \chi_{12}^2 + \chi_{14}^2 + \chi_{24}^2 + \chi_{34}^2}.$$

So also:

$$\lambda_{23} = \mu_{23}$$

$$\lambda_{14} = -\mu_{14}$$

$$\lambda_{31} = \mu_{31}$$

$$\lambda_{24} = -\mu_{24}$$

$$\lambda_{12} = \mu_{12}$$

$$\lambda_{34} = -\mu_{34}$$

or :

$$\left. \begin{aligned} \lambda_{23} + \lambda_{14} &= \mu_{23} - \mu_{14} & \lambda_{23} - \lambda_{14} &= \mu_{23} + \mu_{14} \\ \lambda_{31} + \lambda_{24} &= \mu_{31} - \mu_{24} & \lambda_{31} - \lambda_{24} &= \mu_{31} + \mu_{24} \\ \lambda_{12} + \lambda_{34} &= \mu_{12} - \mu_{34} & \lambda_{12} - \lambda_{34} &= \mu_{12} + \mu_{34} \end{aligned} \right\} \quad (a)$$

Now however

$$\begin{aligned} \lambda_{23} + \lambda_{14} \\ \lambda_{31} + \lambda_{24} \\ \lambda_{12} + \lambda_{34} \end{aligned}$$

are the cosines of direction of the representant of the system of planes equiangular to the right with  $\lambda$  with respect to a system of coordinates  $OX_r Y_r Z_r$  taken in  $S_r$ , as that was defined (These Proceedings Febr. 1904, page 729).

And likewise

$$\begin{aligned} \lambda_{23} - \lambda_{14} \\ \lambda_{31} - \lambda_{24} \\ \lambda_{12} - \lambda_{34} \end{aligned}$$

are the cosines of direction of the representant of the system of planes equiangular to the left with  $\lambda$  with respect to a system of coordinates  $OX_l Y_l Z_l$  taken in an analogous manner in  $S_l$ .

So from the formulae (a) ensues that the effect of a reflection is what we might call a *reciprocal interchange of  $S_r$  and  $S_l$* , i.e. a suchlike interchange that every vector of  $S_l$  takes the place of that vector of  $S_r$  which has substituted itself for it.

But now an arbitrary symmetric transformation of  $S_i$  can be replaced by a reflection preceded or followed by a double rotation: which is represented by a reciprocal interchange of  $S_r$  and  $S_l$  preceded or followed by a rotation of  $S_r$  and one of  $S_l$ ; therefore:

The arbitrary symmetric transformation of  $S_i$  is represented by an *interchange of  $S_r$  and  $S_l$  in arbitrary positions*.

Let us now consider that for such an arbitrary interchange of  $S_r$  and  $S_l$  a system of coordinates  $\alpha$  of  $S_r$  is placed on a system of coordinates  $\beta$  of  $S_l$  whilst that system of coordinates  $\beta$  of  $S_l$  itself is placed on a system  $\gamma$  of  $S_r$ ; then we can replace the interchange by a "reciprocal interchange" placing  $\alpha$  on  $\beta$  and  $\beta$  on  $\alpha$ , followed by a rotation of  $S_r$ , placing  $\alpha$  on  $\gamma$ , or also by a rotation of  $S_l$ , placing  $\alpha$  on  $\gamma$ , followed by a reciprocal interchange, placing  $\gamma$  on  $\beta$  and  $\beta$  on  $\gamma$ .

Consequently we have proved:

"An arbitrary symmetric transformation of  $S_i$  can be replaced by a reflection preceded or followed by a double rotation equiangular

to the right and likewise of course by a reflection preceded or followed by a double rotation equiangular to the left."

The plane of rotation of the equiangular double rotation passing through the axis of reflection remains for both parts of the transformation in an unaltered position; it undergoes by the double rotation a congruent transformation and by the reflection a symmetric one.

The plane of rotation of the equiangular double rotation situated in the space perpendicular to the axis of reflection remains also for both parts of the transformation in an unaltered position; it is not transformed at the reflection and undergoes by the double rotation a congruent transformation.

Those two planes of rotation are perpendicular to each other, so that geometrically the wellknown property is proved:

"For symmetric transformation of  $S_4$  about a fixed point one pair of planes remains at its place; and one plane of it is transformed congruently, the other symmetrically."

**Physics.** — "*On the equations of CLAUSIUS and VAN DER WAALS for the mean length of path and the number of collisions.*" By Dr. PH. KOHNSTAMM. (Communicated by Prof. VAN DER WAALS).

Several of the methods proposed for the derivation of the equation of state, make use of formulae for the mean length of path. It is therefore not to be expected that we shall arrive at undoubted results as to the former, so long as the results as to the latter quantity are not concordant. Now it is generally known that VAN DER WAALS has found for the length of path and the number of collisions in a gas with perfectly hard, perfectly elastic spherical molecules:

$$l = \frac{v-b}{\pi ns^2} \frac{\bar{u}}{r} \quad P = \frac{\pi ns^2}{v-b} \frac{1}{r} \dots \dots (1)$$

It does not seem to be so generally known, that CLAUSIUS<sup>1)</sup> and in accordance with him JÄGER<sup>2)</sup> and BOLTZMANN<sup>3)</sup>, have obtained another result, viz:

$$l = \frac{v}{\pi ns^2} \frac{\bar{u}}{r} \frac{1-2\frac{b}{V}}{1-\frac{11}{8}\frac{b}{V}} \quad P = \frac{\pi ns^2}{v} \frac{1-\frac{11}{8}\frac{b}{v}}{1-2\frac{b}{v}} \dots \dots (2)$$

<sup>1)</sup> Kinetische Theorie der Gase, p. 60.

<sup>2)</sup> Wien. Sitzungsber. 105, p. 97.

<sup>3)</sup> BOLTZMANN Gastheorie, p. 164.

It is clear that at least one of these formulae must be wrong and it does not seem doubtful to me that (1) is so. As is known, formula (1) has been found by VAN DER WAALS by applying a correction to CLAUSIUS' original formula <sup>1)</sup>

$$l = \frac{c}{\tau n s^2} \frac{a}{r} \quad P = \frac{\tau n s^2}{v} r \dots \dots \dots (3)$$

Now it is easy to show that *this* correction has been wrongly applied to (3). We can do this without much difficulty either by making the original proof of CLAUSIUS for (3) applicable, taking into account the reasons which lead to the correction in question, or by making use of VAN DER WAALS' reasoning for (1), which leads really to (3). For shortness I shall confine myself here to pointing out the mistake in the train of thought, which led VAN DER WAALS <sup>2)</sup> and after him KORTEWEG <sup>3)</sup> to the application of this correction. This reasoning is chiefly this. First it is demonstrated that formula (3) holds for a gas, the molecules of which are discs of the same diameter and nature as the spheres in question, which discs have further the property to take a position normal to the direction of their relative motion with regard to a molecule, with which they are going to collide. Then it is thus demonstrated that formula (3) must hold for spheres. (I derive this passage from the proof of KORTEWEG <sup>4)</sup>, with which that of VAN DER WAALS agrees perfectly).

“Now, however, the moment has come, to remove the incorrect hypothesis — introduced in § 3 — and replace the discs again by spheres. The consequence of this will not be that the nature of the collisions is changed, for any molecule *M*, which pursuing its way would have reached any disc, will infallibly first reach the surface of the sphere, which we now put in its place. All the molecules will therefore strike against the same molecules, whose discs we have supposed to be cut by their centres; but all these collisions will take place somewhat earlier, in other words, the paths will be shortened.” From this shortening of the mean path follows the increase of the number of collisions, as this number is in inverse ratio to the length of path.

That this reasoning has been able to deceive not only its inventors, but so many after them, is exclusively due to the ambiguous

<sup>1)</sup> Pogg. 105, p. 239.

<sup>2)</sup> Verslagen Kon. Ak. Afd. Natuurk. Tweede reeks, X. 321. Continuität 1899. p. 45 et seq.

<sup>3)</sup> Verslagen Kon. Ak. Afd. Natuurk. Tweede reeks, X. p. 349.

<sup>4)</sup> l. c., p. 355.

use of the word length of path. If we avoid this, every one will see through the mistake; for really the reasoning comes to this: In a certain time a number of particles reach a certain surface  $A$ ; now every particle reaches a surface  $B$  somewhat sooner, so more particles reach  $B$  than  $A$  in the same time. In essentially the same way we might show that more vertical falling raindrops would strike a pointed roof than a flat one of a section of equal area. Nobody will make this mistake, because it is clear that the number of raindrops falling on the roof depends solely on the quantities, which govern the stream of those drops and on the area of the section of the roof. The same holds for the molecules; and the quantities which determine the strength of the stream of molecules are only the velocity of the molecules, the law of the distribution of velocity which is the same, whatever the form be of the molecules, and the number of molecules per unit of volume.

I said already, that the opposed opinion derives its force from the ambiguous use of the word "length of path." We might also justly say of the raindrops that the path which they describe to get from a certain point to the roof, is shortened, when we think the roof pointed. In the same way we may say of the molecules, that the path *from a certain fixed point* to the sphere is shorter than that to the disc, but this does not hold for the *mean* path and of course the latter only is in inverse ratio to the number of collisions. The validity of this reasoning is easy to see by means of any of the seemingly different definitions for the length of path. I shall for shortness, confine myself to that according to which the mean length of path of molecules moving with the velocity  $c$ , is found by examining, how many molecules strike against a certain molecule within a certain interval of time, by adding the paths described by any of those molecules between this collision and the preceding one, and by dividing this sum by the number of those molecules. Let us now determine the mean path of the molecules which strike with a velocity  $c$  from a direction  $PP'$  either against the disc  $S$ , or the spherical surface  $B$  (Fig. 1). We shall call these molecules the molecules of the group in question. The fact that a molecule of the group in question whose last collision before it reached  $B$  or  $S$  took place in a point  $A^1$ ), will have a shorter path to  $B$  than to  $S$ , does not call for discussion. In so far VAN DER WAALS and KORTEWEG are

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<sup>1)</sup> We shall call such a point henceforth the "last point of collision". This is therefore the point where the collision takes place, which makes a molecule pass into the "group in question". The collision with  $B$  or  $S$  makes the molecule leave this group again.

therefore undoubtedly right. But it follows by no means from this that also the *mean* path is smaller in the first case. For it is clear,

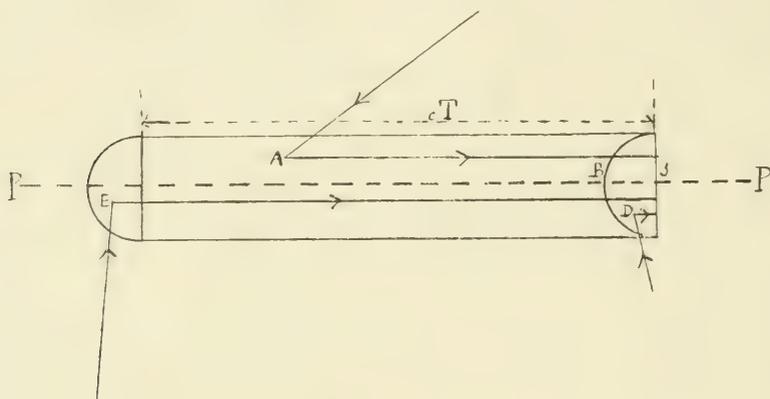


Fig. 1.

that among the molecules of the group in question which in the period  $T$  reach  $S$ , there are some which have their last point of collision close to  $S$ , e.g. in  $D$ . These molecules with their very short path do not count for the group which reach  $B$ . On the other hand there will be others whose last point of collision lies so far from  $B$ , e.g. in  $E$ , that they can reach  $B$ , but not  $S$  in the interval of time  $T$  under consideration; they must therefore be taken into account for  $B$ , but not for  $S$ . That the mean path remains unchanged when we take these circumstances into consideration is best seen by thinking the space, in which the last points of collision lie, divided by planes parallel to  $B$  or  $S$ . It is clear that all molecules which have their last point of collision in parts marked by the same number, (Fig. 2) have the same path; also clear that those points of collision are regularly distributed over the whole volume and that the volume of the parts with the same numbers is the same, so that also the

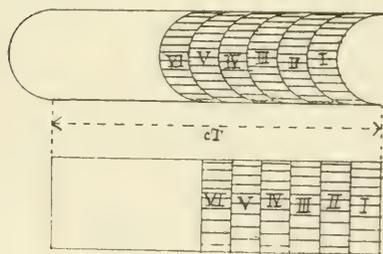


Fig. 2.

mean path must be the same. So if the reason of correction given by VAN DER WAALS were the only one, then the formula (3) would strictly apply unmodified; this is, however, not the case, as there is another reason for correction, which we have not taken into account as yet, as this influence was expressly excluded

by VAN DER WAALS and KORTEWEG in their calculation, by VAN DER

WAALS in the following words <sup>1)</sup>: "This formula --- viz. (1) --- can only hold for the case that the chance that more than two molecules come into collision at the same time may be considered as zero compared to the chance that only two come into collision." KORTEWEG has expressed this more pointedly in the following way <sup>2)</sup>: "For a short time after each collision the possibilities of fresh collisions are considerably influenced by the proximity of the departing molecule. This influence, certainly of very difficult mathematical treatment, is disregarded in my calculations." CLAUSIUS was the first to take this influence into account <sup>3)</sup>, through which he came to formula (2). I will discuss his proof here, as it may lead to a closer approximated value of the length of path, even in principle to the drawing up of a strictly accurate equation, which we shall want for the derivation of the equation of state.

CLAUSIUS (loc. cit.) considers the general case of a point moving in a volume  $W$  between several surfaces in rest. He calculates the chance, that the point will strike against a surface element with the velocity  $dl$ , by considering the point for a moment as stationary, and by giving the surface element the opposite velocity. If  $\theta$  is the angle of the normal to the element with the direction of motion, then the chance that the point lies in the cylindre  $\cos \theta ds dl$ , is equal to  $\frac{\cos \theta ds dl}{W}$ . If we bring this in connection with the chance that such an angle  $\theta$  occurs, and if we integrate over all the angles, we find for the total chance that the element is struck  $\frac{dS}{4W} dl$ , so for the total surface  $\frac{S}{4W} dl$ ; if the mean velocity is  $\bar{u}$ , so  $dl = \bar{u} dt$  then :

$$P = \frac{S\bar{u}}{4W} \quad l = \frac{4W}{S\bar{u}}.$$

This derivation appears to be strictly accurate, as long as all surface elements have an equal chance of being struck and all volume elements have an equal chance of containing the point. If there should be elements for which this chance is zero, they must not be included in the integration. If we think the surfaces to be movable, then it is clear, that we must introduce the mean relative velocity in the way known.

<sup>1)</sup> l. c. p. 336.

<sup>2)</sup> Nature 45 p. 152.

<sup>3)</sup> Pogg. Ergbd. 7 p. 244, cf. Kinetische Theorie der Gase l. c.

From this general formula CLAUSIUS could easily determine  $P$  and  $l$  also for our case. He has only to take into account that in a collision the centre of a molecule must necessarily be on the surface of the distance sphere of the other. If we, therefore, want to determine the number of collisions of the former, we need only see how great the chance is that this molecule will strike against the surface formed by the distance spheres.

We get then:

$$l = \frac{v}{\pi n s^2} \frac{\bar{u}}{r} \quad P = \frac{\pi n s^2}{r}$$

CLAUSIUS observes, however, that not all surface elements can be struck by the moving point, viz. not those which are found within distance spheres. In the same way we must subtract from the volume  $v$  the volume lying within the distance spheres. By determining the area of these surface elements by first approximation, CLAUSIUS obtains:

$$l = \frac{v}{\pi n s^2} \frac{\bar{u}}{r} \frac{1 - 2 \frac{b}{v}}{1 - \frac{11}{8} \frac{b}{v}} \quad P = \frac{\pi n s^2}{v} \frac{1 - \frac{11}{8} \frac{b}{v}}{1 - 2 \frac{b}{v}} \dots \dots (2)$$

It is clear that the fraction  $\frac{1 - 2 \frac{b}{v}}{1 - \frac{11}{8} \frac{b}{v}}$  occurring in these formulae

is only the first approximation of the more general

$$\frac{\text{available volume}}{\text{free surface of distance spheres}} \dots \dots \dots \frac{\text{total}}{\text{total}}$$

If we wish to determine this fraction more accurately we must add to the denominator of this fraction the surface which is found within two distance spheres at the same time, as this quantity has been twice instead of once subtracted in the term  $\frac{11}{8} \frac{b}{v}$ ; when determining this fraction we have namely assumed that all distance spheres fall outside each other. But this is not the whole term of the order  $\frac{b^2}{v^2}$ , as BOLTZMANN<sup>1)</sup> has shown, for in the determination of the

<sup>1)</sup> These Proc. I p. 348.

quantity  $\frac{11}{8} \frac{b}{v}$  we have made a supposition which only holds when neglecting the terms with  $\frac{b^2}{v^2}$ .

We must further add to the numerator the volume of the distance spheres, lying within other distance spheres, which quantity has been twice instead of once subtracted in the term  $2b$ . We get then the form

$$\beta = \frac{1 - \frac{11}{8} \frac{b}{v} + B \frac{b^2}{v^2} + \dots + N \frac{b^n}{v^n}}{1 - 2 \frac{b}{v} + \frac{17}{16} \frac{b^2}{v^2} + C_1 \frac{b^3}{v^3} + \dots + N_1 \frac{b^n}{v^n}} \quad \dots \quad (4)^1$$

where  $n$  is a finite number; for a point cannot lie in more than a finite number of distance spheres at the same time; as VAN LAAR<sup>2)</sup> has made probable, in not more than twelve. We must however keep in view, that the quantity  $v$  which occurs in  $\beta$ , does not represent the *volume*  $v$  but the *available* volume and that this quantity would therefore have to be determined from the equation of the  $n^{\text{th}}$  degree:

$$v_n = v - 2b + \frac{17}{16} \frac{b^2}{v_n} + C_1 \frac{b^3}{v_n^2} \dots + N_1 \frac{b^n}{v_n^{n-1}}$$

There is not much to be said about the coefficients, occurring in the quantity  $\beta$ . As BOLTZMANN<sup>3)</sup> has shown they need not change their signs, on account of the circumstance mentioned by him, as we should expect if we did not take this circumstance into account. So is e.g. as BOLTZMANN has shown,  $C_1$  not negative, but positive. For the present there is not much chance that further coefficients will be determined on account of the exceedingly laborious calculations, which would have to be carried out. Yet formula (4) may already in this form be of use for the question of the derivation of the equation of state.

<sup>1)</sup> The developments of BOLTZMANN's theory of Gas, p. 148 et seq. further continued, lead to the same form.

<sup>2)</sup> Arch. TEYLER (2) VII last page.

<sup>3)</sup> These Proc. I p. 390.

**Physics.** — “On VAN DER WAALS’ equation of state,” by Dr. PH. KOHNSTAMM. (Communicated by Prof. VAN DER WAALS).

§ 1. The way, in which we have to take the extension of molecules into account for the derivation of the equation of state, has been repeatedly a subject of discussion. It is known that, in order to avoid the introduction of repulsive elastic forces and therefore the apparent contradiction with the supposition that only attractive forces act, VAN DER WAALS has, in the first derivation of his equation, not allowed for this extension by means of the virial, but by quite other means. This departure from the path first taken was disapproved of by MAXWELL<sup>1)</sup>, and strongly condemned by TAIT<sup>2)</sup>, who himself from the equation of the virial had arrived at an equation of state, as also LORENTZ had derived. viz.:

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{v} \left(1 + \frac{b}{v}\right) \dots \dots \dots (1)$$

More than ten years ago an interesting controversy was carried on between TAIT<sup>2)</sup>, RAYLEIGH<sup>3)</sup> and KORTEWEG<sup>4)</sup> on the value of this form in comparison with the original form:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \dots \dots \dots (2)$$

Whereas TAIT considered an equation of the form (1) as the only correct one and the derivation of VAN DER WAALS as decidedly wrong, because it could never lead to this form, KORTEWEG thought that he could prove, that on the contrary the final result ought to have form (2), a form which he greatly preferred. This preference, which is not to be justified from a purely mathematical point of view as the two formulae are identical when we take only the terms of the order  $\frac{b}{v}$  into account — and the terms of higher order are neglected in both cases — may be easily understood when we consider that we have here to do with physical problems. For whereas from the form (1) neither the existence of a minimum volume, nor

1) Nature **10**, p. 477.

2) Nature **44**, p. 546, 627; **45**, 199.

3) Nature **44**, p. 499, 597; **45**, 80.

4) Nature **45**, p. 152, 277.

that of a critical point can be derived<sup>1)</sup>, it is known that equation (2) indicates both, though not numerically accurate; one of the numerous cases, where the equation of VAN DER WAALS is a safe guide for the qualitative course of the phenomena, though it is unable to represent them quantitatively. KORTEWEG derives, therefore, from the equation (1), (2)<sup>2)</sup> by putting as it was deduced by VAN DER WAALS

and himself  $P = \frac{\sqrt{2\pi}ms^2}{r-b}$  for the value for the number of collisions instead of  $P = \frac{\sqrt{2\pi}ms^2}{v}$ , which value was used by TAIT and LORENTZ.

This discussion has not led to a perfect agreement, any more than a later discussion carried on between BOLTZMANN<sup>3)</sup> and VAN DER WAALS<sup>4)</sup> about the corrections, which are to be applied to the value of  $b$ , which is put constant in (1) and (2) and equal to the fourfold of the volume of the molecules. As is known, JÄGER<sup>5)</sup> and BOLTZMANN<sup>6)</sup>

found by first approximation  $b_v = b_\infty \left(1 + \frac{5}{8} \frac{b}{r}\right)$  for the  $b$  from (1);

VAN DER WAALS  $b_r = b_\infty \left(1 - \frac{17}{32} \frac{b}{r}\right)$  for that from (2); afterwards

VAN DER WAALS Jr.<sup>7)</sup> has found for the latter  $b_r = b_\infty \left(1 - \frac{3}{8} \frac{b}{r}\right)$

in a different way, so that his result, as far as the terms of the order  $\frac{b}{r}$  and  $\frac{b^2}{r^2}$  are concerned, agrees with that of JÄGER and BOLTZMANN. In

his publications which have appeared since<sup>8)</sup>, his father has pronounced himself "inclined to acknowledge  $\frac{3}{8}$  as the correct value," but it is not doubtful for an attentive reader, that this "inclination" leaves ample room for doubt, both with regard to the value of the coefficient  $\frac{3}{8}$ , and to the following coefficient  $\beta$ , which was given on one side as 0.0958, on the other side as 0.0369.

1) Evidently TAIT has not seen this, but he thinks that the peculiarity of form (2) exists in this, that it is a cubic with respect to  $v$ ; evidently on account of the part which the three sections of the isotherm with a line parallel to the  $v$ -axis, play in the theory of VAN DER WAALS. But he overlooked, that every valid equation of state will have to represent these three volumes.

2) See also VAN DER WAALS: Continuität 1899, p. 60.

3) These Proc. I, p. 398.

4) These Proc. I, p. 468.

5) Wien. Sitzungsber. 105, p. 15.

6) Gastheorie, p. 152.

7) These Proc. 5, p. 487.

8) These Proc. 6, p. 135.

Now it has clearly appeared of late, of how preponderating an importance the knowledge of these corrections is for an accurate equation of state. In the first place BRINKMAN<sup>1)</sup> has succeeded in proving, that the behaviour of air at 0° between 1 and 3000 atms. can be very accurately represented by means of coefficients which do not differ considerably from the values found by BOLTZMANN; then VAN DER WAALS<sup>2)</sup> has proved — as VAN LAAR<sup>3)</sup> had done before — that with the aid of these corrections the critical coefficient becomes  $\left(\frac{RT}{pv}\right)_c = 3.6$  and in this way one of the great discrepancies between theory and experiment seems to be removed. And this last result makes it again clear, how great from a physical point of view, the difference is between an equation of form (1) and (2), though from a mathematical point of view they may be identical by first, second and further approximation. Already a long time ago DIETERICI<sup>4)</sup> proved, as lately HAPPEL<sup>5)</sup> has also done, that with an equation of the form:

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{v} \left\{ 1 + \frac{b}{v} + \alpha \frac{b^2}{v^2} + \dots \right\} \dots \dots (3)$$

the critical coefficient can reach at the utmost the value 3 with the theoretical values of the coefficients, and that this form can therefore never represent the experimental data. It seems therefore not devoid of interest to me, to examine the different derivations of the equation of state, in order to find which form must be taken as the correct one. This investigation will at the same time enable us to form an opinion about the difference between BOLTZMANN and VAN DER WAALS.

§ 2. As is well-known, the proof which VAN DER WAALS originally gave for his equation of state, rests on two theorems, the first of which is explicitly stated, the other is assumed without argument as self-evident. The first theorem states, that the number of collisions in a gas with spherical molecules is represented by the before-mentioned formula  $P = \frac{\sqrt{2}\pi n s^2}{v-b}$ . Now I have already pointed out in a former paper<sup>6)</sup>, that this formula is inaccurate, and must

1) These Proc. VI, p. 510.

2) BOLTZMANN-Festschrift, p. 305.

3) Archives Teyler (2) VII.

4) Wied. 69, p. 685.

5) Drude 13, p. 352.

6) These Proc. p. 787.

be changed by first approximation into  $P = \frac{\sqrt{2}\pi ns^2}{v} \frac{1 - \frac{11b}{8v}}{1 - 2\frac{b}{v}}$  or

neglecting the terms of higher order  $P = \frac{\sqrt{2}\pi ns^2}{v} \left( 1 + \frac{5b}{8v} \right)$ .

The other theorem says that the pressure on the wall (or an imaginary partition) is inversely proportionate to the mean length of path. Already KORTEWEG<sup>1)</sup> has felt an objection to this theorem, and has therefore looked for another way of deriving the equation of state; though convinced of the validity of the theorem, VAN DER WAALS<sup>2)</sup> has later on given another proof, because he considered this theorem as a not to be proved dictum. After the appearance of the already cited paper by VAN DER WAALS JR., however, it is in my opinion beyond doubt, that this theorem does not contain an unprovable truth, but — at least in the terms given here — a provable untruth. For it says the same thing as the statement, that the pressure exerted by the collisions on the distance-spheres per plane unity is equal to that on an imaginary or real wall. It seems to me, however, that VAN DER WAALS JR. has convincingly proved, that when the terms of the order  $\frac{b}{v}$  are taken into account, the relation between these

pressures defined in the usual way, is  $1 - \frac{3b}{8v}$ .

If this result is combined with the just mentioned value for the number of collisions, which determine the pressure on the distance-spheres, it is seen, that also in this way the fourfold of the volume of the molecules is found as first correction, but for the present this does not teach us anything about the final form, because in the communication of VAN DER WAALS JR. the relation of the pressures is not given in its true form, but developed to an infinitely extended series with neglect of the higher powers, which are, however, material to the determination of the final form.

In order to derive the final form, we may, if we want to avoid speaking of repulsive forces, make use of the method based on the increase of the transport of moment brought about by the collisions. We start in this from the observation, that the quantity of motion, which, bound to the molecules, generally moves on with the velocity of them, proceeds in a collision over a certain distance with infinite

1) Verslagen der Kon. Ak. Afd. Natuurk. Tweede reeks, X, p. 362.

2) Continuität 1899, p. 60 cf.

velocity which is best seen by imagining a central shock, in which both molecules pursue their way in the direction from which they came, but adopting each other's motion. It is therefore just as if they have passed through each other with infinite velocity and as if further nothing has happened, so also as if the quantity of motion — of whose motion the pressure of the gas is a consequence — does not move with the velocity of the molecules, but as if with every mean path which is described, a distance is saved, which is a mean of the distances of the centres of the molecules in collisions. If the distance obtained in this way is  $\frac{1}{3} s \sqrt{2}$  for every mean path of  $\frac{r}{\sqrt{2} \pi n s^2}$ , then the increase of the pressure is:

$$\frac{\frac{r}{\sqrt{2} \pi n s^2} + \frac{1}{3} s \sqrt{2}}{r} = 1 + \frac{b}{r}$$

$$\sqrt{2} \pi n s^2$$

If the mean path, when we take into consideration that the distance spheres cover each other, is  $\frac{r}{\sqrt{2} \pi n s^2} \beta$ , where  $\beta = \varphi\left(\frac{b}{r}\right)$ , then the factor which we must take into account is  $1 + \frac{b}{v} \beta$ , and we get the strictly accurate equation:

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{v} \left(1 + \frac{b}{v} \beta\right) \dots \dots \dots (4)$$

The train of thought which we have sketched here in a few words, and from which G. JÄGER (loc. cit.) arrived for the first time at the correction term  $b_0 = b_\infty \left(1 + \frac{5}{8} \frac{b}{v}\right)$  has already been rigorously developed by KORTEWEG<sup>1)</sup>, but he seems to have come to another result. This disagreement is, however, only seeming. KORTEWEG says<sup>2)</sup>: “the sum of all the distances saved by collisions is therefore  $\frac{4}{3} A P v \cos \epsilon dt^3$ ). The sum, however, of all the distances with which the  $P$  molecules approach the plane  $AB$  in the time  $dt$  is evidently  $P v \cos \epsilon dt$ .”

Now it is beyond doubt, in my opinion, that if a number of molecules in the time  $dt$  by their own velocity pass over a way  $P v \cos \epsilon dt$ ,

1) Verslagen der Kon. Ak. Afd. Natuurk. Tweede reeks X p. 362.

2) l. c. p. 369.

3)  $A = \frac{b}{4v}$  in our terminology;  $v$  represents the velocity of the molecules in KORTEWEG's paper.

and at the same time a way  $4APv \cos \epsilon dt$  is saved by the collisions, those molecules seem to move with a velocity  $Pv \cos \epsilon dt(1 + 4A)$ , and so the number of collisions has increased in the same ratio. KORTEWEG, however, continues: "In order to obtain therefore the same number of collisions with the plane  $AB$ , the molecules will only have to pass over a way  $Pv \cos \epsilon dt$ , instead of over a way  $Pv \cos \epsilon (1 - 4A) dt$ , in other words, the number of collisions of this system increases in the ratio  $(1 - 4A):1$ ." Now between the two results there is only difference of order  $\frac{1}{A^2}$  and in so far as we wish to neglect the quantities of this order, KORTEWEG's result may certainly be accepted. If, however, we wish to solve the problem rigorously, the first result alone can be accepted.

For KORTEWEG makes it appear, as if — taking into account the part of the way being saved — an equally long way is described in the time  $(1-4A)dt$ , as in the time  $dt$  without doing so. Now in the last case the molecules pass over a way  $Pv \cos \epsilon dt$  in the time  $dt$ , so  $Pv \cos \epsilon dt(1 - 4A)$  in the time  $(1 - 4A)dt$ . In the time  $dt$  there is saved  $4APv \cos \epsilon dt$ , in the time  $(1 - 4A)dt$  therefore  $(1 - 4A)4APv \cos \epsilon dt$ ; so the distance, passed over in the time  $(1 - 4A)dt$  by saving way and really moving together is somewhat slighter (viz.  $16 A^2 Pv \cos \epsilon dt$ ) than that passed over by the real motion alone in the time  $dt$ ).

<sup>1)</sup> Perhaps KORTEWEG was led when drawing up the formula mentioned in the text by the solution of the problem in one dimension which he has given in *Nature* (loc. cit.) later on. He finds there — perfectly accurately — for the time passing between two collisions against the wall of a row of  $n$  particles of diameter  $\lambda$  which can move over a total distance  $L$  with a velocity  $V$ :

$$T = \frac{L}{L - n\lambda}$$

This formula reminds us more of KORTEWEG's result than of ours, really however it agrees with the latter, not with the former. For, if we determine the ratio of the number of collisions with and without saving way, it is  $Q = \frac{L}{L - n\lambda}$ . Now  $L$  is the total distance over which the molecules can move, so the path described by their own motion + the path saved;  $n\lambda$  is the path saved. So  $L$  corresponds with  $(1 + 4A)Pv \cos \epsilon dt$ ,  $n\lambda$  with  $4APv \cos \epsilon dt$ ; so the ratio of the collisions is here again  $(1 + 4A):1$ . To KORTEWEG's result  $1:(1-4A)$  would the formula  $Q = \frac{L - n\lambda}{L - 2n\lambda}$  correspond, which agrees with the first as to the terms of the order  $\frac{n\lambda}{L}$ , but which is certainly not *strictly* accurate.

It is true that with the formula for one dimension, with regard to its physical meaning, an equation of state agrees, in which a quantity is subtracted from the volume which is a function of  $b$  and  $v$ , not a formula of form (1); but we shall see that our formula derived in the text, leads also to such a final form.

§ 3. So we arrive at equation (4) without making use of the equation of the virial and without speaking of repulsive forces. That the introduction of these and the determination of the so-called "repulsive virial" in the same way as has been done by LORENTZ, TAIT and BOLTZMANN, leads to the same result, is easy to see, if we put everywhere  $\frac{\sqrt{2} \pi n s^2}{v} \beta$  instead of  $\frac{\sqrt{2} \pi n s^2}{v}$  for the number of collisions in the formulae used by them. The expression  $\beta$  does not depend on any of the integrations and the repulsive virial yields therefore  $RT \frac{b}{v} \beta$  instead of  $RT \frac{b}{v}$ . This is easy to understand, even without following the proofs of LORENTZ and BOLTZMANN, for it is clear that the term which is introduced into the equation of the virial through the collisions, must be proportional to the number of those collisions, as two collisions can never be of a different kind<sup>1)</sup>.

It seems therefore as if theory really leads to the form expected by TAIT and DIETERICI, which conforms so little with the experiment. In reality, however, the result is quite different. For — as I pointed out in my other communication —  $\beta$  has by first approximation not the form:  $1 + \frac{5}{8} \frac{b}{v}$ , as JÄGER and BOLTZMANN generally write, but we

find in the way first indicated by CLAUSIUS  $\frac{1 - \frac{11}{8} \frac{b}{v}}{1 - 2 \frac{b}{v}}$  for it, and only

by carrying out the division and by neglecting the terms of higher order, we get the form  $1 + \frac{5}{8} \frac{b}{v}$ . As I showed, we get, taking the terms of higher order into account:

$$\beta = \frac{1 - \frac{11}{8} \frac{b}{v} + B \frac{b^2}{v^2} \dots + N \frac{b^n}{v^n}}{1 - 2 \frac{b}{v} + \frac{17}{16} \frac{b^2}{v^2} + C_1 \frac{b^3}{v^3} \dots + N_1 \frac{b^n}{v^n}} \dots \dots \dots (5)$$

where  $n$  is a finite number.

Now it is true that the other coefficients of this series,  $C_1$  and  $B$  excepted, are unknown, and we might conclude from this, that it must therefore be indifferent for the present, whether the equation of state is written

<sup>1)</sup> KORTEWEG and VAN DER WAALS have also made use of this property in their derivation of equation (2) from (1), mentioned on p. 795.

$$\left( p + \frac{a}{v^2} \right) = \frac{RT}{v} \left\{ 1 + \frac{b - \frac{11}{8} \frac{b^2}{v} + B \frac{b^3}{v^2} + C \frac{b^4}{v^3}}{v - 2b + \frac{17}{16} \frac{b^2}{v} + C_1 \frac{b^3}{v^2}} \right\} \dots (6)$$

or

$$\left( p + \frac{a}{v^2} \right) = \frac{RT}{v} \left\{ 1 + \frac{b}{v} + \frac{5}{8} \frac{b^2}{v^2} + \beta \frac{b^3}{v^3} \right\} \dots (7)$$

but this conclusion would be unjustifiable. For it is possible, nay even probable, that the coefficients of numerator and denominator in (6) decrease rapidly; it is therefore possible, that the true form is accurately represented by a quotient of two forms, which have each only three or four terms; from this follows by no means, that also in the form (7) we should get a close approximation with three or four terms, for the coefficients of the higher powers in (7) do not depend only on the coefficients of the *higher* powers in numerator and denominator of (6), but they are also functions of the coefficients of the lower powers  $1; \frac{11}{8}; 2; \frac{17}{16}$ ; and in such a way that they do not become zero, when the coefficients of the higher powers in (6) do so. Now the difference between (6) and (7) vanishes, of course, for such large values of  $v$ , that the series (7) converges strongly, but for the critical volume and even more so for liquid volumes the difference is very pronounced. This appears already from the simple fact, that a form as (6) can easily yield a minimum volume: but (7) only when an infinite number of terms is taken into account. And also the before mentioned difference between the results of DIETERICI on one side, and VAN LAAR and VAN DER WAALS on the other side, prove how careful we must be with the introduction of simplifications which seem perfectly allowable.

§ 4. Also the other ways proposed for finding the equation of state, arrive at similar final results.

This is easy to see for the most direct way, indicated by BOLTZMANN<sup>1)</sup>. For it is clear, that his formula (4), which leads to the form:

$$\left( p + \frac{a}{v^2} \right) \frac{v - 2b}{1 - \frac{b}{v}} = RT \dots (8)$$

requires another correction on account of the fact that the distance spheres cover each other partially. The numerator of this fraction

<sup>1)</sup> Gastheorie p. 9.

becomes then identical with the denominator of the fraction from (5). In the denominator we get a correction for the part of the cylindre  $\gamma$ , which falls within more than one distance sphere, or as we may also say, for the part of a surface  $A$ , which is found within more than one distance sphere, if we define this surface  $A$  by the condition, that it is found everywhere at a distance  $s$  from the outer surface. We shall call this surface  $A$  henceforth "surface of impact", because the force which in a collision acts on the centres of the molecules, acts in this surface. The determination of the numerical value of the further coefficients seems an exceedingly elaborate work, at least BOLTZMANN announced already in the LORENTZ volume of the Arch. Néerl. that he would have this calculation carried out for the next coefficient, but this calculation has not yet been published. It seems, however not doubtful to me, that also the numerical value must be the same as the value found in other ways. At all events the final form becomes also by this method

$$\left( p + \frac{a}{r^2} \right) \left( \frac{v - 2b + \frac{17}{16} \frac{b^2}{r} + \dots + N_1 \frac{b^n}{r^{n-1}}}{1 - \frac{b}{r} + \beta \frac{b^2}{r^2} + \gamma \frac{b^3}{r^3} \dots + r \frac{b^n}{r^n}} \right) = RT \dots (9)$$

in which  $n$  represents a finite number.

Now it is not difficult to show that the only remaining method for deriving the equation of state, which led to the correction  $^{17}/_{32}$ , must lead to exactly the same equation as (9), when its principles are consistently applied. As is known, this method assumes, that the pressure is to be integrated not only over the volume  $v$ , but also over half of that of the distance spheres:  $b$ , because a molecule whose centre has got on a distance sphere, is subjected to exactly the same force as when it has got on the surface of impact (the volume enclosed by the surface of impact may be put  $= v$ ). The volume of the distance spheres, however, is really smaller than  $\tilde{b}$ , because some distance spheres coincide, and we get therefore<sup>1)</sup>:

$$\left( p + \frac{a}{r^2} \right) \left( v - b + \frac{17}{32} \frac{b^2}{r} \dots \right) = RT \dots (10)$$

NOW VAN DER WAALS JR. (loc. cit.) has already pointed out, that it is tacitly assumed here, that the surface of the distance sphere which is found within another distance sphere experiences a pressure  $= 0$ , and that therefore, for the sake of consequence, also the parts of the surface of impact falling within distance spheres, must be supposed

1) Continuität 1899, p. 65.

to experience a pressure = 0. He has, however, not worked out this thought further; as it seems to me, because he has not fully appreciated the ideas which led his father to the correction  $^{17}/_{32}$ . He has, therefore, substituted for this view, another, undoubtedly correct one, but he has not explained, how the former might be completed in order to yield also the true result. If, however, we make use of the observation made by him, then it is clear that the pressure which seems to be  $P = p + \frac{a}{p^2}$  per unit of surface when we think it as working in the usual way on the total area of the surface of impact  $O$ , must be really larger in the gas, viz. equal to  $p' = P \frac{O}{O'}$ , when this pressure  $p'$  acts only on the *free* surface  $O'$ .

Now it is clear that this quantity  $\frac{O}{O'}$ , which hereby gets into the denominator of the first member of the equation of state is identical with the quantity introduced by BOLTZMANN in this place. For he, too, determines this denominator by examining what part of the surface of impact falls within the distance spheres. This shows us at the same time another point. In the few words which VAN DER WAALS<sup>1)</sup> bestows on this derivation of the equation of state, he says, that the pressure is not to be integrated over the total volume of the distance spheres, as we might expect, but over half of it. Now I have been struck with this from the beginning, and I have tried to find the reason in vain. It appears from what precedes that we have really to integrate over the total volume and that VAN DER WAALS has only introduced the division by two as compensation for the circumstance overlooked by him, but which we take here into account. So he got  $v-b$ , instead of  $\frac{v-2b}{v-b}$ , which evidently does not make any difference by first approximation. But already the second approximation cannot properly be found in this way.

It appears now, that we must integrate the pressure  $p'$ , determined in the way above indicated, over the whole outer surface, that of the distance spheres included in so far as they fall outside each other<sup>2)</sup>, and that

1) Continuität 1899, p. 62.

2) The logical inference from this theorem: that the true equation of state is found by assuming that every surface element, lying either on a plane or a curved wall, experiences a pressure:  $p'$  per unit of surface provided it does not lie within a distance sphere, in which case the pressure must be put equal to 0, would involve, that we did not integrate the pressure over the available volume (volume diminished by the free volume of the distance spheres), but that another correction was applied

the axiom from which VAN DER WAALS started, viz. that we must equate the pressure on the distance spheres and that on the outer wall, is true, if only we apply it to the pressure  $p'$ . This result is only in apparent contradiction with the result of VAN DER WAALS JR., that the pressure  $\bar{P}$  on a fixed plane wall stands to the pressure  $P'$  on the distance spheres in the ratio of  $1 : 1 - \frac{3}{8} \frac{b}{v}$ . For these pressures  $P$  and  $P'$  have been found by supposing the quantity of moment furnished by the wall (and the distance spheres) in the collisions to be distributed over the *total* surface, so by assuming that every surface element contributes an equal amount to the impulse; the pressure  $p'$  of which there is question here, and which proved to be the same for both, is found on the other hand by supposing, that only the mean *free* surface contributes to the quantity of motion, and that the rest is therefore subjected to a pressure = 0.

From this follows:

$$P' = p' \frac{\text{free area of surface of impact}}{\text{total area of surface of impact}} = p' \left( 1 - \frac{b}{v} \right)$$

$$P' = p' \frac{\text{free surface of distance spheres}}{\text{total surface of distance spheres}} = p' \left( 1 - \frac{11}{8} \frac{b}{v} \right)$$

and so  $\frac{P'}{P} = \frac{1 - \frac{11}{8} \frac{b}{v}}{1 - \frac{b}{v}} = 1 - \frac{3}{8} \frac{b}{v}$  with neglect of the terms of higher

order.

The importance of the proof completed in this way, lies for me in the fact, that it makes use of the idea of systems of molecules whose intra-molecular forces need not be introduced into the equation of the virial, provided we adopt the pressure integrated over the whole volume of these systems in the virial. I need not point out the great advantages of such a point of view, already cursorily mentioned by VAN DER WAALS in his dissertation, and later worked out; the communications of VAN DER WAALS on the equation of state and the theory of cyclic motion are striking evidences of its value.

Now it is true that there is a difference between our case and the cases, to which this view is applied in the communications

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in connection with the volume of the distance spheres, which are cut by the surface of impact. This correction would come to an increase of the volume to be integrated with that part of the distance spheres that is found between the surface of impact and the outer wall, but it is clear that this volume may be neglected with the same right as the total volume enclosed by those two surfaces.

mentioned. For in the latter we suppose the existence of really permanent systems of atoms, whereas in our case two molecules whose distance spheres cover each other partially, and which are therefore thought as a system, remain only together for an exceedingly short time. But we see that we get to the right result by assuming, that also the part of the surface of impact lying within the distance spheres, is part of a "system", and that therefore the force exerted on it, does not count<sup>1)</sup>. This result is a priori by no means improbable, for this part of the surface of impact has exactly the same essential property as the other parts of "systems" viz. of falling within distance spheres, whereas in the communications mentioned this hypothesis for the surface of impact was not necessary, because there the systems are characterized by other properties which do not distinguish the surface of impact viz. that it is part of the same system for a comparatively long time.

§ 5. The result obtained in the preceding §, enables us now to use also the first method of reasoning of VAN DER WAALS for the determination of the final form without making use of the virial. For we have seen that the pressure  $P$  on the wall, when the pressure on the distance spheres  $P'$  is determined by

$$\frac{P}{P'} = \frac{\frac{\text{free}}{\text{total}} \text{ area of surface of impact}}{\frac{\text{free}}{\text{total}} \text{ surface of distance spheres}} \dots \dots (10)$$

Now the pressure on the distance spheres is, as appears from CLAUSIUS' formula for the length of path, proportional to:

$$\frac{\frac{\text{free}}{\text{total}} \text{ surface of distance spheres}}{\text{available volume}}$$

so that we find from this for  $P$ :

$$P = f' \frac{\frac{\text{free}}{\text{total}} \text{ area of the surface of impact}}{\text{available volume}}$$

<sup>1)</sup> The real significance of the introduction of these systems may be expressed in this way, that we think the situation of one given moment as fixed, and take into account the systems of more than one distance sphere formed in this way. This removes also what is paradoxal in the supposition (see v. D. WAALS JR. loc. cit. p. 644) that the pressure is 0 in those places which have just experienced a collision or will soon experience one, viz. the points in the distance spheres. For in this fixed state those points are really exempted from collisions from all *other* molecules than those belonging to their system, and whose pressure may therefore be considered as an intra-molecular force.

The signification of  $f'$  we find by equating the volume of the molecules to zero; it appears then, that  $f' = RT$ , so that the equation of state becomes

$$P \frac{\frac{\text{free}}{\text{total}} \text{ available volume}}{\text{area of surface of impact}} = RT$$

identical with (9).

Equation (10) shows us at the same time, what is the physical significance of the quantities used by VAN DER WAALS JR. in his proof with the aid of the virial. For he integrates the pressure  $P$  over the volume  $v$ , the pressure  $P'$  over the volume  $b$ , so that the equation of state becomes:

$$\left( P + \frac{a}{v^2} \right) \left( v - b \frac{\frac{\text{free}}{\text{total}} \text{ surface distance spheres}}{\frac{\text{free}}{\text{total}} \text{ area of surface of impact}} \right) = RT \quad \dots (11)$$

which is, moreover, at once seen, when we read the cited paper attentively. (Specially p. 492).

Though it is not clear to me, why we must integrate here over half the volume of the distance spheres, I must acknowledge that the result — to which we can also get without the proof in question by simply putting the results (6) and (9) identical — is correct. For calculations formula (11) which agrees closest with the original form of VAN DER WAALS, may be of use. I had hoped that I should be able to use the formula obtained in this way for removing the remaining discrepancies between experiment and theory, at least partially, specially the great difference in the value of  $\left( \frac{T}{P} \frac{dP}{dT} \right)_c$ .

As yet these efforts have not met with the desired success, and it is obvious, that this will not be possible, before we know e.g. the numerator of (11) much more accurately than we do now. It is clear that this numerator in virtue of its physical signification, can never become zero for volumes larger than the minimum volume; now we know this numerator only in the shape  $1 - \frac{11}{8} \frac{b}{v}$ , an expression which becomes zero for very much larger volumes, nay even for the ordinary liquid volumes. For these volumes therefore the application of the correction  $1 - \frac{11}{8} \frac{b}{v}$  will be injurious, instead of advantageous. Not before the mathematical form of two of the three quan-

ties :  $\frac{\text{free}}{\text{total}}$  surface distance spheres ;  $\frac{\text{free}}{\text{total}}$  area of surface of impact : available volume, is more accurately known, we shall be justified in expecting better concordance of experiment and theory.

**Physics.** — “*Note on SYDNEY YOUNG’S law of distillation.*” By MISS J. REUDLER. (Communicated by Prof. J. D. VAN DER WAALS).

Some time ago SYDNEY YOUNG gave a law of fractional distillation<sup>1)</sup>, which seems very strange at first sight. According to this law in distillations with an efficient still, the weight of distillate coming over below the middle point of the boiling temperatures of the components would be almost equal to the weight of the most volatile component, also when the separation is far from perfect. This concordance would be so close, that YOUNG could even base a general law of quantitative analysis on it, at least for substances whose boiling points were not too near to each other. Now it seemed, however, unlikely, that this law should always hold, quite independent of the nature of the *T<sub>v</sub>*-curves and of the composition of the mixture from which we start. Therefore I have distilled some mixtures, inter alia also with YOUNG’S evaporator still head.

I began with some of the examples chosen by YOUNG, and I found really that they confirmed the law. Then I tried to determine the limits of its validity by taking a mixture with very steep *T<sub>v</sub>*-line, so that I could closely examine, what happens, when the distillation is broken off above or below the mean boiling point. I took for this benzene (boiling point 79°,6) and aniline (boiling point 180°) and began with such a composition, that the initial boiling point lay already above the middle point, thinking that YOUNG’S law would be sure not to hold in this case. Yet also now the law was confirmed, but the process of the distillation revealed also the character of the rule. For it appeared that independent of the composition of the mixture, even when it consisted of 4 % benzene and 96 % aniline, and so a thermometer, which I had placed in the liquid, pointed to almost 180° already in the beginning of the distillation, the temperature in the still head remained constant at 79° for a long time, and rose then suddenly very rapidly to 180°, so that the distillation might have been broken off with the same result very far above and

<sup>1)</sup> J. Chem. Soc. 81 752.

below the middle point 129 °S. It appeared in other words, that with YouNG's still head an almost perfect separation was reached already in a single distillation. That the law under consideration holds in this case, is self-evident.

I found also there where the  $T_x$ -line is less steep, as for benzene and toluene, that the thermometer remained in the neighbourhood of the boiling point of the most volatile substance during the greater part of the distillation, and then suddenly rose rapidly, quickly passing through the middle temperature, so that here too the breaking off at the middle temperature is not essential.

Where it is essential as with distillations with less efficient still head or for mixtures with very flat  $T_x$ -line, the law does not hold. As an instance I give the three following distillations, the first of which, where a mixture with very steep  $T_x$ -line is distilled with the evaporator, conforms to the law; whereas the second, where the same mixture is distilled with an ordinary straight tube and specially the third where a mixture with flat  $T_x$ -line is distilled with the evaporator, deviate from the law.

Still head.	Component	Boiling point	Weight of the components in gr.	Come over below middle temp. in gr.
Evaporator	Benzene	79°,6	60,8	60,6
	Toluene	110°,8	54,6	
Straight tube	Benzene	79°,6	50,0	46,2
	Toluene	110°,8	50,0	
Evaporator	Carbon tetrachlorate	77°,0	71,4	407,7
	Benzene	79°,6	98,3	

In accordance with this YouNG himself gives his law only for mixtures which are not difficult to separate distilled with an efficient still head.

I think that I am justified in concluding that the law is simply based on the separation of the mixture in its components, and that we have to include under what YouNG calls: a far from perfect separation, only those cases, where at the end of the distillation a small fraction of the most volatile substance is left in the recipient

and a small fraction of the least volatile is present in the distillate. That the two quantities will then differ little in weight and therefore the deviation from the law is comparatively small, is not strange in my opinion.

I think to have shown in this way, that YOUNG'S rule is a proof of the excellent way in which YOUNG'S still heads work, but that from a point of view of quantitative analysis we must only take this rule as an application of the most obvious operation, viz that of separating a substance in pure state from a mixture and then weighing it separately.

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**Physics.** — “*Electromagnetic phenomena in a system moving with any velocity smaller than that of light.*” By Prof. H. A. LORENTZ.

§ 1. The problem of determining the influence exerted on electric and optical phenomena by a translation, such as all systems have in virtue of the Earth's annual motion, admits of a comparatively simple solution, so long as only those terms need be taken into account, which are proportional to the first power of the ratio between the velocity of translation  $w$  and the velocity of light  $c$ .

Cases in which quantities of the second order, i.e. of the order  $\frac{w^2}{c^2}$ , may be perceptible, present more difficulties. The first example of this kind is MICHELSON'S well known interference-experiment, the negative result of which has led FITZ GERALD and myself to the conclusion that the dimensions of solid bodies are slightly altered by their motion through the aether.

Some new experiments in which a second order effect was sought for have recently been published. RAYLEIGH <sup>1)</sup> and BRACE <sup>2)</sup> have examined the question whether the Earth's motion may cause a body to become doubly refracting; at first sight this might be expected, if the just mentioned change of dimensions is admitted. Both physicists have however come to a negative result.

In the second place TROUTON and NOBLE <sup>3)</sup> have endeavoured to detect a turning couple acting on a charged condenser, whose plates make a certain angle with the direction of translation. The theory

<sup>1)</sup> RAYLEIGH, Phil. Mag. (6) 4 (1902), p. 678.

<sup>2)</sup> BRACE, Phil. Mag. (6) 7 (1904), p. 317.

<sup>3)</sup> TROUTON and NOBLE, London Roy. Soc. Trans. A 202 (1903), p. 165.

of electrons, unless it be modified by some new hypothesis, would undoubtedly require the existence of such a couple. In order to see this, it will suffice to consider a condenser with aether as dielectricum. It may be shown that in every electrostatic system, moving with a velocity  $w$ <sup>1)</sup>, there is a certain amount of "electromagnetic momentum". If we represent this, in direction and magnitude, by a vector  $\mathfrak{G}$ , the couple in question will be determined by the vector product <sup>2)</sup>

$$[\mathfrak{G} \cdot w] \dots \dots \dots (1)$$

Now, if the axis of  $z$  is chosen perpendicular to the condenser plates, the velocity  $w$  having any direction we like, and if  $U$  is the energy of the condenser, calculated in the ordinary way, the components of  $\mathfrak{G}$  are given <sup>3)</sup> by the following formulae, which are exact up to the first order:

$$\mathfrak{G}_x = \frac{2U}{c^2} w_x, \mathfrak{G}_y = \frac{2U}{c^2} w_y, \mathfrak{G}_z = 0.$$

Substituting these values in (1), we get for the components of the couple, up to terms of the second order,

$$\frac{2U}{c^2} w_y w_z, - \frac{2U}{c^2} w_x w_z, 0.$$

These expressions show that the axis of the couple lies in the plane of the plates, perpendicular to the translation. If  $\alpha$  is the angle between the velocity and the normal to the plates, the moment of the couple will be  $\frac{U}{c^2} w^2 \sin 2\alpha$ ; it tends to turn the condenser into such a position that the plates are parallel to the Earth's motion.

In the apparatus of TROCTON and NOBLE the condenser was fixed to the beam of a torsion-balance, sufficiently delicate to be deflected by a couple of the above order of magnitude. No effect could however be observed.

§ 2. The experiments of which I have spoken are not the only reason for which a new examination of the problems connected with the motion of the Earth is desirable. POINCARÉ<sup>4)</sup> has objected

1) A vector will be denoted by a German letter, its magnitude by the corresponding Latin letter.

2) See my article: Weiterbildung der MAXWELL'schen Theorie. Electronentheorie in the Mathem. Encyclopädie V 14, § 21, a. (This article will be quoted as M. E.)

3) M. E. § 56, c.

4) POINCARÉ, Rapports du Congrès de physique de 1900, Paris, 1, p. 22, 23.

to the existing theory of electric and optical phenomena in moving bodies that, in order to explain MICHELSON'S negative result, the introduction of a new hypothesis has been required, and that the same necessity may occur each time new facts will be brought to light. Surely, this course of inventing special hypotheses for each new experimental result is somewhat artificial. It would be more satisfactory, if it were possible to show, by means of certain fundamental assumptions, and without neglecting terms of one order of magnitude or another, that many electromagnetic actions are entirely independent of the motion of the system. Some years ago, I have already sought to frame a theory of this kind<sup>1)</sup>. I believe now to be able to treat the subject with a better result. The only restriction as regards the velocity will be that it be smaller than that of light.

§ 3. I shall start from the fundamental equations of the theory of electrons<sup>2)</sup>. Let  $\mathfrak{d}$  be the dielectric displacement in the aether,  $\mathfrak{h}$  the magnetic force,  $\mathfrak{q}$  the volume-density of the charge of an electron,  $\mathfrak{v}$  the velocity of a point of such a particle, and  $\mathfrak{f}$  the electric force, i. e. the force, reckoned per unit charge, which is exerted by the aether on a volume-element of an electron. Then, if we use a fixed system of coordinates,

$$\left. \begin{aligned} \operatorname{div} \mathfrak{d} &= \mathfrak{q} \quad , \quad \operatorname{div} \mathfrak{h} = 0, \\ \operatorname{rot} \mathfrak{h} &= \frac{1}{c} (\dot{\mathfrak{d}} + \mathfrak{q} \mathfrak{v}), \\ \operatorname{rot} \mathfrak{d} &= -\frac{1}{c} \dot{\mathfrak{h}}, \\ \mathfrak{f} &= \mathfrak{d} + \frac{1}{c} [\mathfrak{v}, \mathfrak{h}]. \end{aligned} \right\} \dots \dots \dots (2)$$

I shall now suppose that the system as a whole moves in the direction of  $x$  with a constant velocity  $w$ , and I shall denote by  $u$  any velocity a point of an electron may have in addition to this, so that

$$v_x = w + u_x, \quad v_y = u_y, \quad v_z = u_z.$$

If the equations (2) are at the same time referred to axes moving with the system, they become

<sup>1)</sup> LORENTZ, Zittingsverslag Akad. v. Wet., 7 (1899), p. 507; Amsterdam Proc., 1898—99, p. 427.

<sup>2)</sup> M. E., § 2.

$$\operatorname{div} \mathfrak{d} = \rho, \quad \operatorname{div} \mathfrak{h} = 0,$$

$$\frac{\partial \mathfrak{h}_z}{\partial y} - \frac{\partial \mathfrak{h}_y}{\partial z} = \frac{1}{c} \left( \frac{\partial}{\partial t} - w \frac{\partial}{\partial x} \right) \mathfrak{d}_x + \frac{1}{c} \rho (v + u_x),$$

$$\frac{\partial \mathfrak{h}_x}{\partial z} - \frac{\partial \mathfrak{h}_z}{\partial x} = \frac{1}{c} \left( \frac{\partial}{\partial t} - w \frac{\partial}{\partial x} \right) \mathfrak{d}_y + \frac{1}{c} \rho u_y,$$

$$\frac{\partial \mathfrak{h}_y}{\partial x} - \frac{\partial \mathfrak{h}_x}{\partial y} = \frac{1}{c} \left( \frac{\partial}{\partial t} - w \frac{\partial}{\partial x} \right) \mathfrak{d}_z + \frac{1}{c} \rho u_z,$$

$$\frac{\partial \mathfrak{d}_z}{\partial y} - \frac{\partial \mathfrak{d}_y}{\partial z} = -\frac{1}{c} \left( \frac{\partial}{\partial t} - w \frac{\partial}{\partial x} \right) \mathfrak{h}_x,$$

$$\frac{\partial \mathfrak{d}_x}{\partial z} - \frac{\partial \mathfrak{d}_z}{\partial x} = -\frac{1}{c} \left( \frac{\partial}{\partial t} - w \frac{\partial}{\partial x} \right) \mathfrak{h}_y,$$

$$\frac{\partial \mathfrak{d}_y}{\partial x} - \frac{\partial \mathfrak{d}_x}{\partial y} = -\frac{1}{c} \left( \frac{\partial}{\partial t} - w \frac{\partial}{\partial x} \right) \mathfrak{h}_z,$$

$$\mathfrak{f}_x = \mathfrak{d}_x + \frac{1}{c} (u_y \mathfrak{h}_z - u_z \mathfrak{h}_y),$$

$$\mathfrak{f}_y = \mathfrak{d}_y - \frac{1}{c} w \mathfrak{h}_z + \frac{1}{c} (u_z \mathfrak{h}_x - u_x \mathfrak{h}_z),$$

$$\mathfrak{f}_z = \mathfrak{d}_z + \frac{1}{c} w \mathfrak{h}_y + \frac{1}{c} (u_x \mathfrak{h}_y - u_y \mathfrak{h}_x).$$

§ 4. We shall further transform these formulae by a change of variables. Putting

$$\frac{c^2}{c^2 - w^2} = k^2. \quad \dots \dots \dots (3)$$

and understanding by  $l$  another numerical quantity, to be determined further on, I take as new independent variables

$$x' = k l x, \quad y' = l y, \quad z' = l z, \quad \dots \dots \dots (4)$$

$$t' = \frac{l}{k} t - k l \frac{w}{c^2} x, \quad \dots \dots \dots (5)$$

and I define two new vectors  $\mathfrak{d}'$  and  $\mathfrak{h}'$  by the formulae

$$\mathfrak{d}'_x = \frac{1}{l^2} \mathfrak{d}_x, \quad \mathfrak{d}'_y = \frac{k}{l^2} \left( \mathfrak{d}_y - \frac{w}{c} \mathfrak{h}_z \right), \quad \mathfrak{d}'_z = \frac{k}{l^2} \left( \mathfrak{d}_z + \frac{w}{c} \mathfrak{h}_y \right),$$

$$\mathfrak{h}'_x = \frac{1}{l^2} \mathfrak{h}_x, \quad \mathfrak{h}'_y = \frac{k}{l^2} \left( \mathfrak{h}_y + \frac{w}{c} \mathfrak{d}_z \right), \quad \mathfrak{h}'_z = \frac{k}{l^2} \left( \mathfrak{h}_z - \frac{w}{c} \mathfrak{d}_y \right),$$

for which, on account of (3), we may also write

$$\left. \begin{aligned} \mathfrak{d}_x &= l^2 \mathfrak{d}'_x, \quad \mathfrak{d}_y = k l^2 \left( \mathfrak{d}'_y + \frac{w}{c} \mathfrak{h}'_z \right), \quad \mathfrak{d}_z = k l^2 \left( \mathfrak{d}'_z - \frac{w}{c} \mathfrak{h}'_y \right) \\ \mathfrak{h}_x &= l^2 \mathfrak{h}'_x, \quad \mathfrak{h}_y = k l^2 \left( \mathfrak{h}'_y - \frac{w}{c} \mathfrak{d}'_z \right), \quad \mathfrak{h}_z = k l^2 \left( \mathfrak{h}'_z + \frac{w}{c} \mathfrak{d}'_y \right) \end{aligned} \right\} \quad (6)$$

As to the coefficient  $l$ , it is to be considered as a function of  $w$ , whose value is 1 for  $w = 0$ , and which, for small values of  $w$ , differs from unity no more than by an amount of the second order.

The variable  $t'$  may be called the "local time"; indeed, for  $k = 1$ ,  $l = 1$  it becomes identical with what I have formerly understood by this name.

If, finally, we put

$$\frac{1}{k l^2} \varrho = \varrho', \dots \dots \dots (7)$$

$$k^2 u_x = u'_x, \quad k u_y = u'_y, \quad k u_z = u'_z, \dots \dots \dots (8)$$

these latter quantities being considered as the components of a new vector  $u'$ , the equations take the following form:

$$\left. \begin{aligned} \operatorname{div}' \mathfrak{d}' &= \left(1 - \frac{w u'_x}{c^2}\right) \varrho', \quad \operatorname{div}' \mathfrak{h}' = 0, \\ \operatorname{rot}' \mathfrak{h}' &= \frac{1}{c} \left(\frac{\partial \mathfrak{d}'}{\partial t'} + \varrho' u'\right), \\ \operatorname{rot}' \mathfrak{d}' &= -\frac{1}{c} \frac{\partial \mathfrak{h}'}{\partial t'}. \end{aligned} \right\} \dots \dots \dots (9)$$

$$\left. \begin{aligned} \mathfrak{f}_x &= l^2 \mathfrak{d}'_x + l^2 \cdot \frac{1}{c} (u'_y \mathfrak{h}'_z - u'_z \mathfrak{h}'_y) + l^2 \cdot \frac{w}{c^2} (u'_y \mathfrak{d}'_y + u'_z \mathfrak{d}'_z), \\ \mathfrak{f}_y &= \frac{l^2}{k} \mathfrak{d}'_y + \frac{l^2}{k} \cdot \frac{1}{c} (u'_z \mathfrak{h}'_x - u'_x \mathfrak{h}'_z) - \frac{l^2}{k} \cdot \frac{w}{c^2} u'_x \mathfrak{d}'_y, \\ \mathfrak{f}_z &= \frac{l^2}{k} \mathfrak{d}'_z + \frac{l^2}{k} \cdot \frac{1}{c} (u'_x \mathfrak{h}'_y - u'_y \mathfrak{h}'_x) - \frac{l^2}{k} \cdot \frac{w}{c^2} u'_x \mathfrak{d}'_z. \end{aligned} \right\} \dots \dots \dots (10)$$

The meaning of the symbols  $\operatorname{div}'$  and  $\operatorname{rot}'$  in (9) is similar to that of  $\operatorname{div}$  and  $\operatorname{rot}$  in (2); only, the differentiations with respect to  $x, y, z$  are to be replaced by the corresponding ones with respect to  $x', y', z'$ .

§ 5. The equations (9) lead to the conclusion that the vectors  $\mathfrak{d}'$  and  $\mathfrak{h}'$  may be represented by means of a scalar potential  $\varphi'$  and a vector potential  $\mathfrak{a}'$ . These potentials satisfy the equations<sup>1)</sup>

$$\Delta' \varphi' - \frac{1}{c^2} \frac{\partial^2 \varphi'}{\partial t'^2} = -\varrho', \dots \dots \dots (11)$$

$$\Delta' \mathfrak{a}' - \frac{1}{c^2} \frac{\partial^2 \mathfrak{a}'}{\partial t'^2} = -\frac{1}{c} \varrho' u'. \dots \dots \dots (12)$$

and in terms of them  $\mathfrak{d}'$  and  $\mathfrak{h}'$  are given by

<sup>1)</sup> M. E., §§ 4 and 10.

$$\mathfrak{v}' = - \frac{1}{c} \frac{\partial \mathfrak{a}'}{\partial t'} - \mathit{grad}' \mathfrak{q}' + \frac{w}{c} \mathit{grad}' \mathfrak{a}', \dots \dots \dots (13)$$

$$\mathfrak{b}' = \mathit{rot}' \mathfrak{a}', \dots \dots \dots (14)$$

The symbol  $\mathcal{L}'$  is an abbreviation for  $\frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2}$ , and  $\mathit{grad}' \mathfrak{q}'$  denotes a vector whose components are  $\frac{\partial \mathfrak{q}'}{\partial x'}, \frac{\partial \mathfrak{q}'}{\partial y'}, \frac{\partial \mathfrak{q}'}{\partial z'}$ . The expression  $\mathit{grad}' \mathfrak{a}'$  has a similar meaning.

In order to obtain the solution of (11) and (12) in a simple form, we may take  $x', y', z'$  as the coordinates of a point  $P'$  in a space  $S'$ , and ascribe to this point, for each value of  $t'$ , the values of  $\mathfrak{q}', \mathfrak{u}', \mathfrak{q}', \mathfrak{a}'$ , belonging to the corresponding point  $P(x, y, z)$  of the electromagnetic system. For a definite value  $t'$  of the fourth independent variable, the potentials  $\mathfrak{q}'$  and  $\mathfrak{a}'$  in the point  $P$  of the system or in the corresponding point  $P'$  of the space  $S'$ , are given by<sup>1)</sup>

$$\mathfrak{q}' = \frac{1}{4\pi\epsilon_0} \int \frac{[\mathfrak{q}']}{r'} dS', \dots \dots \dots (15)$$

$$\mathfrak{a}' = \frac{1}{4\pi\epsilon_0} \int \frac{[\mathfrak{q}'\mathfrak{u}']}{r'} dS', \dots \dots \dots (16)$$

Here  $dS'$  is an element of the space  $S'$ ,  $r'$  its distance from  $P'$  and the brackets serve to denote the quantity  $\mathfrak{q}'$  and the vector  $\mathfrak{q}'\mathfrak{u}'$ , such as they are in the element  $dS'$ , for the value  $t' = \frac{r'}{c}$  of the fourth independent variable.

Instead of (15) and (16) we may also write, taking into account (4) and (7).

$$\mathfrak{q}' = \frac{1}{4\pi\epsilon_0} \int \frac{[\mathfrak{q}]}{r} dS, \dots \dots \dots (17)$$

$$\mathfrak{a}' = \frac{1}{4\pi\epsilon_0} \int \frac{[\mathfrak{q}\mathfrak{u}]}{r} dS, \dots \dots \dots (18)$$

the integrations now extending over the electromagnetic system itself. It should be kept in mind that in these formulae  $r'$  does not denote the distance between the element  $dS$  and the point  $(x, y, z)$  for which the calculation is to be performed. If the element lies at the point  $(x_1, y_1, z_1)$ , we must take

$$r' = r \sqrt{k^2 (x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2}.$$

It is also to be remembered that, if we wish to determine  $\mathfrak{q}'$  and

<sup>1)</sup> M. E., §§ 5 and 10.

$\mathfrak{a}'$  for the instant, at which the local time in  $P$  is  $t'$ , we must take  $\varrho$  and  $\varrho u'$ , such as they are in the element  $dS$  at the instant at which the local time of that element is  $t' - \frac{r'}{c}$ .

§ 6. It will suffice for our purpose to consider two special cases. The first is that of an electrostatic system, i. e. a system having no other motion but the translation with the velocity  $w$ . In this case  $u' = 0$ , and therefore, by (12),  $\mathfrak{a}' = 0$ . Also,  $\varrho'$  is independent of  $t'$ , so that the equations (11), (13) and (14) reduce to

$$\left. \begin{aligned} \mathcal{L}' \varphi' &= -\varrho', \\ \mathfrak{d}' &= -grad' \varphi', \mathfrak{b}' = 0. \end{aligned} \right\} \dots \dots \dots (19)$$

After having determined the vector  $\mathfrak{d}'$  by means of these equations, we know also the electric force acting on electrons that belong to the system. For these the formulae (10) become, since  $u' = 0$ ,

$$\mathfrak{f}_x = l^2 \mathfrak{d}'_x, \mathfrak{f}_y = \frac{l^2}{k} \mathfrak{d}'_y, \mathfrak{f}_z = \frac{l^2}{k} \mathfrak{d}'_z. \dots \dots \dots (20)$$

The result may be put in a simple form if we compare the moving system  $\Sigma$  with which we are concerned, to another electrostatic system  $\Sigma'$  which remains at rest and into which  $\Sigma$  is changed, if the dimensions parallel to the axis of  $x$  are multiplied by  $kl$ , and the dimensions which have the direction of  $y$  or that of  $z$ , by  $l$ , a deformation for which  $(kl, l, l)$  is an appropriate symbol. In this new system, which we may suppose to be placed in the above mentioned space  $S'$ , we shall give to the density the value  $\varrho'$ , determined by (7), so that the charges of corresponding elements of volume and of corresponding electrons are the same in  $\Sigma$  and  $\Sigma'$ . Then we shall obtain the forces acting on the electrons of the moving system  $\Sigma$ , if we first determine the corresponding forces in  $\Sigma'$ , and next multiply their components in the direction of the axis of  $x$  by  $l^2$ , and their components perpendicular to that axis by  $\frac{l^2}{k}$ . This is conveniently expressed by the formula

$$\mathfrak{F}(\Sigma) = \left( l^2, \frac{l^2}{k}, \frac{l^2}{k} \right) \mathfrak{F}(\Sigma') \dots \dots \dots (21)$$

It is further to be remarked that, after having found  $\mathfrak{d}'$  by (19), we can easily calculate the electromagnetic momentum in the moving system, or rather its component in the direction of the motion. Indeed, the formula

$$\mathfrak{G} = \frac{1}{c} \int [\mathfrak{d} \cdot \mathfrak{b}] dS$$

shows that

$$\mathfrak{G}_x = \frac{1}{c} \int (\mathfrak{d}_y \mathfrak{b}_z - \mathfrak{d}_z \mathfrak{b}_y) dS$$

Therefore, by (6), since  $\mathfrak{b}' = 0$

$$\mathfrak{G}_x = \frac{k^2 l^3 w}{c^2} \int (\mathfrak{d}_y'^2 + \mathfrak{d}_z'^2) dS = \frac{klw}{c^2} \int (\mathfrak{d}_y'^2 + \mathfrak{d}_z'^2) dS'. \quad (22)$$

§ 7. Our second special case is that of a particle having an electric moment, i. e. a small space  $S$ , with a total charge  $\int \mathfrak{q} dS = 0$ , but with such a distribution of density, that the integrals  $\int \mathfrak{q} x dS$ ,  $\int \mathfrak{q} y dS$ ,  $\int \mathfrak{q} z dS$  have values differing from 0.

Let  $\mathbf{x}$ ,  $\mathbf{y}$ ,  $\mathbf{z}$  be the coordinates, taken relatively to a fixed point  $A$  of the particle, which may be called its centre, and let the electric moment be defined as a vector  $\mathfrak{p}$  whose components are

$$\mathfrak{p}_x = \int \mathfrak{q} \mathbf{x} dS, \quad \mathfrak{p}_y = \int \mathfrak{q} \mathbf{y} dS, \quad \mathfrak{p}_z = \int \mathfrak{q} \mathbf{z} dS. \quad (23)$$

Then

$$\frac{d\mathfrak{p}_x}{dt} = \int \mathfrak{q} u_x dS, \quad \frac{d\mathfrak{p}_y}{dt} = \int \mathfrak{q} u_y dS, \quad \frac{d\mathfrak{p}_z}{dt} = \int \mathfrak{q} u_z dS. \quad (24)$$

Of course, if  $\mathbf{x}$ ,  $\mathbf{y}$ ,  $\mathbf{z}$  are treated as infinitely small,  $u_x$ ,  $u_y$ ,  $u_z$  must be so likewise. We shall neglect squares and products of these six quantities.

We shall now apply the equation (17) to the determination of the scalar potential  $\varphi'$  for an exterior point  $P(x, y, z)$ , at finite distance from the polarized particle, and for the instant at which the local time of this point has some definite value  $t'$ . In doing so, we shall give the symbol  $[\mathfrak{q}]$ , which, in (17), relates to the instant at which the local time in  $dS$  is  $t' - \frac{r'}{c}$ , a slightly different meaning. Distinguishing by  $r'_0$  the value of  $r'$  for the centre  $A$ , we shall understand by  $[\mathfrak{q}]$  the value of the density existing in the element  $dS$  at the point  $(\mathbf{x}, \mathbf{y}, \mathbf{z})$ , at the instant  $t_0$  at which the local time of  $A$  is  $t' - \frac{r'_0}{c}$ .

It may be seen from (5) that this instant precedes that for which we have to take the numerator in (17) by

$$k^2 \frac{w}{c^2} \mathbf{x} + \frac{k}{l} \frac{r'_0 - r'}{c} = k^2 \frac{w}{c^2} \mathbf{x} + \frac{k}{l} \frac{1}{c} \left( \mathbf{x} \frac{\partial r'}{\partial x} + \mathbf{y} \frac{\partial r'}{\partial y} + \mathbf{z} \frac{\partial r'}{\partial z} \right)$$

units of time. In this last expression we may put for the differential coefficients their values at the point  $A$ .

In (17) we have now to replace  $[q]$  by

$$[q] + k^2 \frac{w}{c^2} \mathbf{x} \left[ \frac{\partial q}{\partial t} \right] + \frac{k}{l} \frac{1}{c} \left( \mathbf{x} \frac{\partial r'}{\partial x} + \mathbf{y} \frac{\partial r'}{\partial y} + \mathbf{z} \frac{\partial r'}{\partial z} \right) \left[ \frac{\partial q}{\partial t} \right], \quad (25)$$

where  $\left[ \frac{\partial q}{\partial t} \right]$  relates again to the time  $t_0$ . Now, the value of  $t'$  for which the calculations are to be performed having been chosen, this time  $t_0$  will be a function of the coordinates  $x, y, z$  of the exterior point  $P$ . The value of  $[q]$  will therefore depend on these coordinates in such a way that

$$\frac{\partial [q]}{\partial x} = - \frac{k}{l} \frac{1}{c} \frac{\partial r'}{\partial x} \left[ \frac{\partial q}{\partial t} \right], \text{ etc.,}$$

by which (25) becomes

$$[q] + k^2 \frac{w}{c^2} \mathbf{x} \left[ \frac{\partial q}{\partial t} \right] - \left( \mathbf{x} \frac{\partial [q]}{\partial x} + \mathbf{y} \frac{\partial [q]}{\partial y} + \mathbf{z} \frac{\partial [q]}{\partial z} \right).$$

Again, if henceforth we understand by  $r'$  what has above been called  $r'_0$ , the factor  $\frac{1}{r'}$  must be replaced by

$$\frac{1}{r'} - \mathbf{x} \frac{\partial}{\partial x} \left( \frac{1}{r'} \right) - \mathbf{y} \frac{\partial}{\partial y} \left( \frac{1}{r'} \right) - \mathbf{z} \frac{\partial}{\partial z} \left( \frac{1}{r'} \right),$$

so that after all, in the integral (17), the element  $dS$  is multiplied by

$$\frac{[q]}{r'} + k^2 \frac{w}{c^2} \frac{\mathbf{x}}{r'} \left[ \frac{\partial q}{\partial t} \right] - \frac{\partial}{\partial x} \frac{\mathbf{x} [q]}{r'} - \frac{\partial}{\partial y} \frac{\mathbf{y} [q]}{r'} - \frac{\partial}{\partial z} \frac{\mathbf{z} [q]}{r'}.$$

This is simpler than the primitive form, because neither  $r'$ , nor the time for which the quantities enclosed in brackets are to be taken, depend on  $x, y, z$ . Using (23) and remembering that  $\int q dS = 0$ , we get

$$p' = k^2 \frac{w}{4 \pi c^2 r'} \left[ \frac{\partial \mathbf{r}_x}{\partial t} \right] - \frac{1}{4 \pi} \left\{ \frac{\partial}{\partial x} \left[ \frac{\mathbf{r}_x}{r'} \right] + \frac{\partial}{\partial y} \left[ \frac{\mathbf{r}_y}{r'} \right] + \frac{\partial}{\partial z} \left[ \frac{\mathbf{r}_z}{r'} \right] \right\},$$

a formula in which all the enclosed quantities are to be taken for the instant at which the local time of the centre of the particle is  $t' - \frac{r'}{c}$ .

We shall conclude these calculations by introducing a new vector  $\mathbf{p}'$ , whose components are

$$p'_x = kl p_x, p'_y = l p_y, p'_z = l p_z, \dots \quad (26)$$

passing at the same time to  $x', y', z', t'$  as independent variables. The final result is

$$\varphi' = \frac{w}{4\pi c^2 r'} \frac{\partial [p'_x]}{\partial t'} - \frac{1}{4\pi} \left\{ \frac{\partial [p'_x]}{\partial x'} \frac{1}{r'} + \frac{\partial [p'_y]}{\partial y'} \frac{1}{r'} + \frac{\partial [p'_z]}{\partial z'} \frac{1}{r'} \right\}.$$

As to the formula (18) for the vector potential, its transformation is less complicate, because it contains the infinitely small vector  $u'$ . Having regard to (8), (24), (26) and (5), I find

$$a' = \frac{1}{4\pi c r'} \frac{\partial [p']}{\partial t'}.$$

The field produced by the polarized particle is now wholly determined. The formula (13) leads to

$$b' = - \frac{1}{4\pi c^2 \partial t'^2} \frac{\partial^2 [p']}{\partial t'^2} + \frac{1}{4\pi} \text{grad}' \left\{ \frac{\partial [p'_x]}{\partial x'} \frac{1}{r'} + \frac{\partial [p'_y]}{\partial y'} \frac{1}{r'} + \frac{\partial [p'_z]}{\partial z'} \frac{1}{r'} \right\} \quad (27)$$

and the vector  $b'$  is given by (14). We may further use the equations (20), instead of the original formulae (10), if we wish to consider the forces exerted by the polarized particle on a similar one placed at some distance. Indeed, in the second particle, as well as in the first, the velocities  $u$  may be held to be infinitely small.

It is to be remarked that the formulae for a system without translation are implied in what precedes. For such a system the quantities with accents become identical to the corresponding ones without accents; also  $k=1$  and  $l=1$ . The components of (27) are at the same time those of the electric force which is exerted by one polarized particle on another.

§ 8. Thus far we have only used the fundamental equations without any new assumptions. I shall now suppose *that the electrons, which I take to be spheres of radius  $R$  in the state of rest, have their dimensions changed by the effect of a translation, the dimensions in the direction of motion becoming  $kl$  times and those in perpendicular directions  $l$  times smaller.*

In this deformation, which may be represented by  $\left(\frac{1}{kl}, \frac{1}{l}, \frac{1}{l}\right)$ , each element of volume is understood to preserve its charge.

Our assumption amounts to saying that in an electrostatic system  $\Sigma$ , moving with a velocity  $w$ , all electrons are flattened ellipsoids with their smaller axes in the direction of motion. If now, in order to apply the theorem of § 6, we subject the system to the deformation  $(kl, l, l)$ , we shall have again spherical electrons of radius  $R$ ,

Hence, if we alter the relative position of the centres of the electrons in  $\Sigma$  by applying the deformation  $(kl, l, l)$ , and if, in the points thus obtained, we place the centres of electrons that remain at rest, we shall get a system, identical to the imaginary system  $\Sigma'$ , of which we have spoken in § 6. The forces in this system and those in  $\Sigma$  will bear to each other the relation expressed by (21).

In the second place I shall suppose *that the forces between uncharged particles, as well as those between such particles and electrons, are influenced by a translation in quite the same way as the electric forces in an electrostatic system.* In other terms, whatever be the nature of the particles composing a ponderable body, so long as they do not move relatively to each other, we shall have between the forces acting in a system ( $\Sigma'$ ) without, and the same system ( $\Sigma$ ) with a translation, the relation specified in (21), if, as regards the relative position of the particles,  $\Sigma'$  is got from  $\Sigma$  by the deformation  $(kl, l, l)$ , or  $\Sigma$  from  $\Sigma'$  by the deformation  $\left(\frac{1}{kl}, \frac{1}{l}, \frac{1}{l}\right)$ .

We see by this that, as soon as the resulting force is 0 for a particle in  $\Sigma'$ , the same must be true for the corresponding particle in  $\Sigma$ . Consequently, if, neglecting the effects of molecular motion, we suppose each particle of a solid body to be in equilibrium under the action of the attractions and repulsions exerted by its neighbours, and if we take for granted that there is but one configuration of equilibrium, we may draw the conclusion that the system  $\Sigma'$ , if the velocity  $w$  is imparted to it, will *of itself* change into the system  $\Sigma$ . In other terms, the translation will *produce* the deformation  $\left(\frac{1}{kl}, \frac{1}{l}, \frac{1}{l}\right)$ .

The case of molecular motion will be considered in § 12.

It will easily be seen that the hypothesis that has formerly been made in connexion with MICHELSON'S experiment, is implied in what has now been said. However, the present hypothesis is more general because the only limitation imposed on the motion is that its velocity be smaller than that of light.

§ 9. We are now in a position to calculate the electromagnetic momentum of a single electron. For simplicity's sake I shall suppose the charge  $e$  to be uniformly distributed over the surface, so long as the electron remains at rest. Then, a distribution of the same kind will exist in the system  $\Sigma'$  with which we are concerned in the last integral of (22). Hence

$$\int (\delta + \delta^2) dS = \frac{2}{3} \int \delta^2 dS = \frac{e^2}{6\pi} \int_R^{\infty} \frac{dr}{r^2} = \frac{e^2}{6\pi R}$$

and

$$\mathfrak{G}_r = \frac{e^2}{6\pi c^2 R} k l w.$$

It must be observed that the product  $kl$  is a function of  $w$  and that, for reasons of symmetry, the vector  $\mathfrak{G}$  has the direction of the translation. In general, representing by  $w$  the velocity of this motion, we have the vector equation

$$\mathfrak{G} = \frac{e^2}{6\pi c^2 R} k l w. \quad (28)$$

Now, every change in the motion of a system will entail a corresponding change in the electromagnetic momentum and will therefore require a certain force, which is given in direction and magnitude by

$$\mathfrak{F} = \frac{d\mathfrak{G}}{dt}. \quad (29)$$

Strictly speaking, the formula (28) may only be applied in the case of a uniform rectilinear translation. On account of this circumstance — though (29) is always true — the theory of rapidly varying motions of an electron becomes very complicated, the more so, because the hypothesis of § 8 would imply that the direction and amount of the deformation are continually changing. It is even hardly probable that the form of the electron will be determined solely by the velocity existing at the moment considered.

Nevertheless, provided the changes in the state of motion be sufficiently slow, we shall get a satisfactory approximation by using (28) at every instant. The application of (29) to such a *quasi-stationary* translation, as it has been called by ABRAHAM <sup>1)</sup>, is a very simple matter. Let, at a certain instant,  $j_1$  be the acceleration in the direction of the path, and  $j_2$  the acceleration perpendicular to it. Then the force  $\mathfrak{F}$  will consist of two components, having the directions of these accelerations and which are given by

$$\mathfrak{F}_1 = m_1 j_1 \quad \text{and} \quad \mathfrak{F}_2 = m_2 j_2,$$

if

$$m_1 = \frac{e^2}{6\pi c^2 R} \frac{d(k l w)}{d w} \quad \text{and} \quad m_2 = \frac{e^2}{6\pi c^2 R} k l. \quad (30)$$

Hence, in phenomena in which there is an acceleration in the

<sup>1)</sup> ABRAHAM, Wied. Ann. 10 (1903), p. 105.

direction of motion, the electron behaves as if it had a mass  $m_1$ , in those in which the acceleration is normal to the path, as if the mass were  $m_2$ . These quantities  $m_1$  and  $m_2$  may therefore properly be called the "longitudinal" and "transverse" electromagnetic masses of the electron. I shall suppose *that there is no other, no "true" or "material" mass.*

Since  $k$  and  $l$  differ from unity by quantities of the order  $\frac{w^2}{c^2}$ , we find for very small velocities

$$m_1 = m_2 = \frac{e^2}{6\pi c^2 R}.$$

This is the mass with which we are concerned, if there are small vibratory motions of the electrons in a system without translation. If, on the contrary, motions of this kind are going on in a body moving with the velocity  $w$  in the direction of the axis of  $x$ , we shall have to reckon with the mass  $m_1$ , as given by (30), if we consider the vibrations parallel to that axis, and with the mass  $m_2$ , if we treat of those that are parallel to  $OY$  or  $OZ$ . Therefore, in short terms, referring by the index  $\Sigma$  to a moving system and by  $\Sigma'$  to one that remains at rest,

$$m(\Sigma) = \left( \frac{d(klw)}{dw}, kl, kl \right) m(\Sigma') . . . . . (31)$$

§ 10. We can now proceed to examine the influence of the Earth's motion on optical phenomena in a system of transparent bodies. In discussing this problem we shall fix our attention on the variable electric moments in the particles or "atoms" of the system. To these moments we may apply what has been said in § 7. For the sake of simplicity we shall suppose that, in each particle, the charge is concentrated in a certain number of separate electrons, and that the "elastic" forces that act on one of these and, conjointly with the electric forces, determine its motion, have their origin within the bounds of the *same* atom.

I shall show that, if we start from any given state of motion in a system without translation, we may deduce from it a corresponding state that can exist in the same system after a translation has been imparted to it, the kind of correspondence being as specified in what follows.

*a.* Let  $A'_1, A'_2, A'_3$ , etc. be the centres of the particles in the system without translation ( $\Sigma'$ ): neglecting molecular motions we shall take these points to remain at rest. The system of points

$A_1, A_2, A_3$ , etc., formed by the centres of the particles in the moving system  $\Sigma$ , is obtained from  $A'_1, A'_2, A'_3$ , etc. by means of a deformation  $\left(\frac{1}{kl}, \frac{1}{l}, \frac{1}{l}\right)$ . According to what has been said in § 8, the centres

will of themselves take these positions  $A'_1, A'_2, A'_3$ , etc. if originally, before there was a translation, they occupied the positions  $A_1, A_2, A_3$ , etc.

We may conceive any point  $P'$  in the space of the system  $\Sigma'$  to be displaced by the above deformation, so that a definite point  $P$  of  $\Sigma$  corresponds to it. For two corresponding points  $P'$  and  $P$  we shall define corresponding instants, the one belonging to  $P'$ , the other to  $P$ , by stating that the true time at the first instant is equal to the local time, as determined by (5) for the point  $P$ , at the second instant. By corresponding times for two corresponding *particles* we shall understand times that may be said to correspond, if we fix our attention on the *centres*  $A'$  and  $A$  of these particles.

*b.* As regards the interior state of the atoms, we shall assume that the configuration of a particle  $A$  in  $\Sigma$  at a certain time may be derived by means of the deformation  $\left(\frac{1}{kl}, \frac{1}{l}, \frac{1}{l}\right)$  from the configuration of the corresponding particle in  $\Sigma'$ , such as it is at the corresponding instant. In so far as this assumption relates to the form of the electrons themselves, it is implied in the first hypothesis of § 8.

Obviously, if we start from a state really existing in the system  $\Sigma'$ , we have now completely defined a state of the moving system  $\Sigma$ . The question remains however, whether this state will likewise be a possible one.

In order to judge this, we may remark in the first place that the electric moments which we have supposed to exist in the moving system and which we shall denote by  $\mathfrak{p}$ , will be certain definite functions of the coordinates  $x, y, z$  of the centres  $A$  of the particles, or, as we shall say, of the coordinates of the particles themselves, and of the time  $t$ . The equations which express the relations between  $\mathfrak{p}$  on one hand and  $x, y, z, t$  on the other, may be replaced by other equations, containing the vectors  $\mathfrak{p}'$  defined by (26) and the quantities  $x', y', z', t'$  defined by (4) and (5). Now, by the above assumptions *a* and *b*, if in a particle  $A$  of the moving system, whose coordinates are  $x, y, z$ , we find an electric moment  $\mathfrak{p}$  at the time  $t$ , or at the local time  $t'$ , the vector  $\mathfrak{p}'$  given by (26) will be the moment which exists in the other system at the true time  $t'$  in a particle whose coordinates are  $x', y', z'$ . It appears in this way that the equations between  $\mathfrak{p}', x', y', z', t'$  are the same for both systems, the difference being only this, that for the system  $\Sigma'$  without translation

these symbols indicate the moment, the coordinates and the true time, whereas their meaning is different for the moving system,  $x', y', z', t'$  being here related to the moment  $\mathfrak{p}$ , the coordinates  $x, y, z$  and the general time  $t$  in the manner expressed by (26), (4) and (5).

It has already been stated that the equation (27) applies to both systems. The vector  $\mathfrak{d}'$  will therefore be the same in  $\Sigma'$  and  $\Sigma$ , provided we always compare corresponding places and times. However, this vector has not the same meaning in the two cases. In  $\Sigma'$  it represents the electric force, in  $\Sigma$  it is related to this force in the way expressed by (20). We may therefore conclude that the electric forces acting, in  $\Sigma$  and in  $\Sigma'$ , on corresponding particles at corresponding instants, bear to each other the relation determined by (21). In virtue of our assumption *b*, taken in connexion with the second hypothesis of § 8, the same relation will exist between the "elastic" forces; consequently, the formula (21) may also be regarded as indicating the relation between the total forces, acting on corresponding electrons, at corresponding instants.

It is clear that the state we have supposed to exist in the moving system will really be possible if, in  $\Sigma$  and  $\Sigma'$ , the products of the mass  $m$  and the acceleration of an electron are to each other in the same relation as the forces, i. e. if

$$m \mathfrak{j}(\Sigma) = \left( l^2, \frac{l^2}{k}, \frac{l^2}{k} \right) m \mathfrak{j}(\Sigma') \dots \dots \dots (32)$$

Now, we have for the accelerations

$$\mathfrak{j}(\Sigma) = \left( \frac{l}{k^2}, \frac{l}{k^2}, \frac{l}{k^2} \right) \mathfrak{j}(\Sigma'), \dots \dots \dots (33)$$

as may be deduced from (4) and (5), and combining this with (32), we find for the masses

$$m(\Sigma) = (k^3 l, kl, kl) m(\Sigma')$$

If this is compared to (31), it appears that, whatever be the value of  $l$ , the condition is always satisfied, as regards the masses with which we have to reckon when we consider vibrations perpendicular to the translation. The only condition we have to impose on  $l$  is therefore

$$\frac{d(klw)}{dw} = k^3 l.$$

But, on account of (3),

$$\frac{d(kw)}{dw} = k^2,$$

so that we must put

$$\frac{dl}{dv} = 0. \quad l = \text{const.}$$

The value of the constant must be unity, because we know already that, for  $w = 0, l = 1$ .

We are therefore led to suppose *that the influence of a translation on the dimensions (of the separate electrons and of a ponderable body as a whole) is confined to those that have the direction of the motion, these becoming  $k$  times smaller than they are in the state of rest.* If this hypothesis is added to those we have already made, we may be sure that two states, the one in the moving system, the other in the same system while at rest, corresponding as stated above, may both be possible. Moreover, this correspondence is not limited to the electric moments of the particles. In corresponding points that are situated either in the aether between the particles, or in that surrounding the ponderable bodies, we shall find at corresponding times the same vector  $\mathfrak{d}'$  and, as is easily shown, the same vector  $\mathfrak{h}'$ . We may sum up by saying: If, in the system without translation, there is a state of motion in which, at a definite place, the components of  $\mathfrak{p}, \mathfrak{d}$  and  $\mathfrak{h}$  are certain functions of the time, then the same system after it has been put in motion (and thereby deformed) can be the seat of a state of motion in which, at the corresponding place, the components of  $\mathfrak{p}', \mathfrak{d}'$  and  $\mathfrak{h}'$  are the same functions of the local time.

There is one point which requires further consideration. The values of the masses  $m_1$  and  $m_2$  having been deduced from the theory of quasi-stationary motion, the question arises, whether we are justified in reckoning with them in the case of the rapid vibrations of light. Now it is found on closer examination that the motion of an electron may be treated as quasi-stationary if it changes very little during the time a light-wave takes to travel over a distance equal to the diameter. This condition is fulfilled in optical phenomena, because the diameter of an electron is extremely small in comparison with the wave-length.

§ 11. It is easily seen that the proposed theory can account for a large number of facts.

Let us take in the first place the case of a system without translation, in some parts of which we have continually  $\mathfrak{p} = 0, \mathfrak{d} = 0, \mathfrak{h} = 0$ . Then, in the corresponding state for the moving system, we shall have in corresponding parts (or, as we may say, in the same parts of the deformed system)  $\mathfrak{p}' = 0, \mathfrak{d}' = 0, \mathfrak{h}' = 0$ . These equations implying  $\mathfrak{v} = 0, \mathfrak{d} = 0, \mathfrak{h} = 0$ , as is seen by (26) and (6), it appears

that those parts which are dark while the system is at rest, will remain so after it has been put in motion. It will therefore be impossible to detect an influence of the Earth's motion on any optical experiment, made with a terrestrial source of light, in which the geometrical distribution of light and darkness is observed. Many experiments on interference and diffraction belong to this class.

In the second place, if in two points of a system, rays of light of the same state of polarization are propagated in the same direction, the ratio between the amplitudes in these points may be shown not to be altered by a translation. The latter remark applies to those experiments in which the intensities in adjacent parts of the field of view are compared.

The above conclusions confirm the results I have formerly obtained by a similar train of reasoning, in which however the terms of the second order were neglected. They also contain an explanation of MICHELSON'S negative result, more general and of somewhat different form than the one previously given, and they show why RAYLEIGH and BRACE could find no signs of double refraction produced by the motion of the Earth.

As to the experiments of TROUTON and NOBLE, their negative result becomes at once clear, if we admit the hypotheses of § 8. It may be inferred from these and from our last assumption (§ 10) that the only effect of the translation must have been a contraction of the whole system of electrons and other particles constituting the charged condenser and the beam and thread of the torsion-balance. Such a contraction does not give rise to a sensible change of direction.

It need hardly be said that the present theory is put forward with all due reserve. Though it seems to me that it can account for all well established facts, it leads to some consequences that cannot as yet be put to the test of experiment. One of these is that the result of MICHELSON'S experiment must remain negative, if the interfering rays of light are made to travel through some ponderable transparent body.

Our assumption about the contraction of the electrons cannot in itself be pronounced to be either plausible or inadmissible. What we know about the nature of electrons is very little and the only means of pushing our way farther will be to test such hypotheses as I have here made. Of course, there will be difficulties, e.g. as soon as we come to consider the rotation of electrons. Perhaps we shall have to suppose that in those phenomena in which, if there is no translation, spherical electrons rotate about a diameter, the points of the electrons in the moving system will describe elliptic paths,

corresponding, in the manner specified in § 10, to the circular paths described in the other case.

§ 12. It remains to say some words about molecular motion. We may conceive that bodies in which this has a sensible influence or even predominates, undergo the same deformation as the systems of particles of constant relative position of which alone we have spoken till now. Indeed, in two systems of molecules  $\Sigma'$  and  $\Sigma$ , the first without and the second with a translation, we may imagine molecular motions corresponding to each other in such a way that, if a particle in  $\Sigma'$  has a certain position at a definite instant, a particle in  $\Sigma$  occupies at the corresponding instant the corresponding position. This being assumed, we may use the relation (33) between the accelerations in all those cases in which the velocity of molecular motion is very small as compared to  $w$ . In these cases the molecular forces may be taken to be determined by the relative positions, independently of the velocities of molecular motion. If, finally, we suppose these forces to be limited to such small distances that, for particles acting on each other, the difference of local times may be neglected, one of the particles, together with those which lie in its sphere of attraction or repulsion, will form a system which undergoes the often mentioned deformation. In virtue of the second hypothesis of § 8 we may therefore apply to the resulting molecular force acting on a particle, the equation (21). Consequently, the proper relation between the forces and the accelerations will exist in the two cases, if we suppose *that the masses of all particles are influenced by a translation to the same degree as the electromagnetic masses of the electrons.*

§ 13. The values (30) which I have found for the longitudinal and transverse masses of an electron, expressed in terms of its velocity, are not the same as those that have been formerly obtained by ABRAHAM. The ground for this difference is solely to be sought in the circumstance that, in his theory, the electrons are treated as spheres of invariable dimensions. Now, as regards the transverse mass, the results of ABRAHAM have been confirmed in a most remarkable way by KAUFMANN'S measurements of the deflexion of radium-rays in electric and magnetic fields. Therefore, if there is not to be a most serious objection to the theory I have now proposed, it must be possible to show that those measurements agree with my values nearly as well as with those of ABRAHAM.

I shall begin by discussing two of the series of measurements

published by KAUFMANN<sup>1)</sup> in 1902. From each series he has deduced two quantities  $\eta$  and  $\xi$ , the "reduced" electric and magnetic deflexions, which are related as follows to the ratio  $\beta = \frac{w}{c}$ :

$$\beta = k_1 \frac{\xi}{\eta}, \quad \psi(\beta) = \frac{\eta}{k_2 \xi^2} \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Here  $\psi(\beta)$  is such a function, that the transverse mass is given by

$$m_2 = \frac{3}{4} \cdot \frac{e^2}{6\pi c^2 R} \psi(\beta), \quad . \quad . \quad . \quad . \quad . \quad (35)$$

whereas  $k_1$  and  $k_2$  are constant in each series.

It appears from the second of the formulae (30) that my theory leads likewise to an equation of the form (35); only ABRAHAM'S function  $\psi(\beta)$  must be replaced by

$$\frac{4}{3} k = \frac{4}{3} (1 - \beta^2)^{-1/2}.$$

Hence, my theory requires that, if we substitute this value for  $\psi(\beta)$  in (34), these equations shall still hold. Of course, in seeking to obtain a good agreement, we shall be justified in giving to  $k_1$  and  $k_2$  other values than those of KAUFMANN, and in taking for every measurement a proper value of the velocity  $w$ , or of the ratio  $\beta$ . Writing  $s k_1$ ,  $\frac{3}{4} k'_2$  and  $\beta'$  for the new values, we may put (34) in the form

$$\beta' = s k_1 \frac{\xi}{\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

and

$$(1 - \beta'^2)^{-1/2} = \frac{\eta}{k'_2 \xi^2} \quad , \quad . \quad . \quad . \quad . \quad . \quad (37)$$

KAUFMANN has tested his equations by choosing for  $k_1$  such a value that, calculating  $\beta$  and  $k_2$  by means of (34), he got values for this latter number that remained constant in each series as well as might be. This constancy was the proof of a sufficient agreement.

I have followed a similar method, using however some of the numbers calculated by KAUFMANN. I have computed for each measurement the value of the expression

$$k'_2 = (1 - \beta'^2)^{1/2} \psi(\beta) k_2, \quad . \quad . \quad . \quad . \quad . \quad (38)$$

that may be got from (37) combined with the second of the equations (34). The values of  $\psi(\beta)$  and  $k_2$  have been taken from KAUFMANN'S tables and for  $\beta'$  I have substituted the value he has found for  $\beta$ , multiplied by  $s$ , the latter coefficient being chosen with a view to

<sup>1)</sup> KAUFMANN, Physik. Zeitschr. 4 (1902), p. 55.

obtaining a good constancy of (38). The results are contained in the following tables, corresponding to the tables III and IV in KAUFMANN'S paper.

III.  $s = 0,933.$ 

$\beta$	$\psi(\beta)$	$k_2$	$\beta'$	$k_2'$
0,851	2,447	1,721	0,794	2,246
0,766	1,86	1,736	0,715	2,258
0,727	1,78	1,725	0,678	2,256
0,6615	1,66	1,727	0,617	2,256
0,6075	1,595	1,655	0,567	2,175

IV.  $s = 0,954.$ 

$\beta$	$\psi(\beta)$	$k_2$	$\beta'$	$k_2'$
0,963	3,23	8,12	0,919	10,36
0,949	2,86	7,99	0,905	9,70
0,933	2,73	7,46	0,890	9,28
0,883	2,31	8,32	0,842	10,36
0,860	2,195	8,09	0,820	10,15
0,830	2,06	8,13	0,792	10,23
0,801	1,96	8,13	0,764	10,28
0,777	1,89	8,04	0,744	10,20
0,752	1,83	8,02	0,717	10,22
0,732	1,785	7,97	0,698	10,18

The constancy of  $k_2'$  is seen to come out no less satisfactory than that of  $k_2$ , the more so as in each case the value of  $s$  has been determined by means of only two measurements. The coefficient has been so chosen that for these two observations, which were in Table III the first and the last but one, and in Table IV the first and the last, the values of  $k_2'$  should be proportional to those of  $k_2$ .

I shall next consider two series from a later publication by KAUFMANN<sup>1)</sup>, which have been calculated by RUNGE<sup>2)</sup> by means of the method of

1) KAUFMANN, Gött. Nachr. Math. phys. Kl., 1903, p. 90.

2) RUNGE, ibidem, p. 326.

least squares, the coefficients  $k_1$  and  $k_2$  having been determined in such a way, that the values of  $\eta$ , calculated, for each observed  $\zeta$ , from KAUFMANN'S equations (34), agree as closely as may be with the observed values of  $\eta$ .

I have determined by the same condition, likewise using the method of least squares, the constants  $a$  and  $b$  in the formula

$$\eta^2 = a\zeta^2 + b\zeta^4,$$

which may be deduced from my equations (36) and (37). Knowing  $a$  and  $b$ , I find  $\beta$  for each measurement by means of the relation

$$\beta = \sqrt{a} \frac{\zeta}{\eta}.$$

For two plates on which KAUFMANN had measured the electric and magnetic deflexions, the results are as follows, the deflexions being given in centimeters.

I have not found time for calculating the other tables in KAUFMANN'S paper. As they begin, like the table for Plate 15, with a rather large negative difference between the values of  $\eta$  which have been deduced from the observations and calculated by RUNGE, we may expect a satisfactory agreement with my formulae.

§ 14. I take this opportunity for mentioning an experiment that

Plate N°. 15.  $a = 0,06489$ ,  $b = 0,3039$ .

$\zeta$	$\eta$					$\beta$	
	Observed.	Calculated by R.	Diff.	Calculated by L.	Diff.	Calculated by	
						R.	L.
0.1495	0.0388	0.0404	- 16	0.0400	- 12	0.987	0.951
0.199	0.0548	0.0550	- 2	0.0552	- 4	0.964	0.918
0.2475	0.0716	0.0710	+ 6	0.0715	+ 1	0.930	0.881
0.296	0.0896	0.0887	+ 9	0.0895	+ 1	0.889	0.842
0.3435	0.1080	0.1081	- 1	0.1090	- 10	0.847	0.803
0.391	0.1290	0.1297	- 7	0.1305	- 15	0.804	0.763
0.437	0.1524	0.1527	- 3	0.1532	- 8	0.763	0.727
0.4825	0.1788	0.1777	+ 11	0.1777	+ 11	0.724	0.692
0.5265	0.2033	0.2039	- 6	0.2033	0	0.688	0.660

Plate N<sup>o</sup>. 19.  $a = 0,05867$ ,  $b = 0,2591$ .

$\xi$	$\eta$					$\beta$	
	Observed.	Calculated by R.	Diff.	Calculated by L.	Diff.	Calculated by R.      L.	
0.1495	0.0404	0.0388	+ 16	0.0379	+25	0.990	0.954
0.199	0.0529	0.0527	+ 2	0.0522	+ 7	0.969	0.923
0.247	0.0678	0.0675	+ 3	0.0674	+ 4	0.939	0.888
0.296	0.0834	0.0842	- 8	0.0844	-10	0.902	0.849
0.3435	0.1019	0.1022	- 3	0.1026	- 7	0.862	0.811
0.391	0.1219	0.1222	- 3	0.1226	- 7	0.822	0.773
0.437	0.1429	0.1434	- 5	0.1437	- 8	0.782	0.736
0.4825	0.1660	0.1665	- 5	0.1664	- 4	0.744	0.702
0.5265	0.1916	0.1906	+ 10	0.1902	+14	0.709	0.671

has been made by TROUTON<sup>1)</sup> at the suggestion of FITZ GERALD, and in which it was tried to observe the existence of a sudden impulse acting on a condenser at the moment of charging or discharging; for this purpose the condenser was suspended by a torsion-balance, with its plates parallel to the Earth's motion. For forming an estimate of the effect that may be expected, it will suffice to consider a condenser with aether as dielectricum. Now, if the apparatus is charged, there will be (§ 1) an electromagnetic momentum

$$\mathfrak{G} = \frac{2}{c^2} U w.$$

(Terms of the third and higher orders are here neglected). This momentum being produced at the moment of charging, and disappearing at that of discharging, the condenser must experience in the first case an impulse  $-\mathfrak{G}$  and in the second an impulse  $+\mathfrak{G}$ .

However TROUTON has not been able to observe these jerks.

I believe it may be shown (though his calculations have led him to a different conclusion) that the sensibility of the apparatus was far from sufficient for the object TROUTON had in view.

Representing, as before, by  $U$  the energy of the charged condenser

<sup>1)</sup> TROUTON, Dublin Roy. Soc. Trans. (2) 7 (1902), p. 379 (This paper may also be found in The scientific writings of FITZ GERALD, edited by LARMOR, Dublin and London 1902, p. 557).

in the state of rest, and by  $U + U'$  the energy in the state of motion, we have by the formulae of this paper, up to the terms of the second order,

$$U' = \frac{2}{v^2} U,$$

an expression, agreeing in order of magnitude with the value used by TROTTON for estimating the effect.

The intensity of the sudden jerk or impulse will therefore be  $\frac{U'}{r}$ .

Now, supposing the apparatus to be initially at rest, we may compare the deflexion  $\alpha$ , produced by this impulse, to the deflexion  $\alpha'$  which may be given to the torsion-balance by means of a constant couple  $K$ , acting during half the vibration time. We may also consider the case in which a swinging motion has already been set up; then the impulse, applied at the moment in which the apparatus passes through the position of equilibrium, will alter the amplitude by a certain amount  $\beta$  and a similar effect  $\beta'$  may be caused by letting the couple  $K$  act during the swing from one extreme position to the other. Let  $T$  be the period of swinging and  $l$  the distance from the condenser to the thread of the torsion-balance. Then it is easily found that

$$\frac{\alpha}{\alpha'} = \frac{\beta}{\beta'} = \frac{\pi U' l}{K T v} \dots \dots \dots (39)$$

According to TROTTON'S statements  $U'$  amounted to one or two ergs, and the smallest couple by which a sensible deflexion could be produced was estimated at 7,5 C. G. S.-units. If we substitute this value for  $K$  and take into account that the velocity of the Earth's motion is  $3 \times 10^6$  c.M. per sec., we immediately see that (39) must have been a very small fraction.

**Mathematics.** — "*Observation on the paper communicated on Febr. 27<sup>th</sup> 1904 by Mr. BROUWER: "On a decomposition of the continuous motion about a point  $O$  of  $S_4$  into two continuous motions about  $O$  of  $S_3$ 's."* BY DR. E. JAHNKE. (Communicated by Prof. D. J. KORTEWEG.)

The above mentioned paper is connected with investigations of FERD. CASPARY and with works published by me in the years 1896—1901. Mr. BROUWER not referring to these, I take the liberty to remark the following: Problems of the theory of the thetafunctions on one hand and of mechanics on the other hand have led

me to relate the rotation in  $S_4$  to two rotations in  $S_3$ . The relations between the elements of the four-dimensional rotation and the elements of the two three-dimensional rotations belonging to it have been explicitly pointed out by me in "Sitzungsberichte der Berliner Akademie" of July 30<sup>th</sup> 1896 and in the "Journal für die reine und angewandte Mathematik" Vol. 118, p. 215, 1897. I have particularly found that the components of the velocity of the first rotation are easily deduced from the components of the velocity of the two others (compare also my lecture at the "Naturforscher Versammlung" at Hamburg 1901: "On rotations in fourdimensional spaces," (Ueber Drehungen im vierdimensionalen Raum).

Mr. BROUWER arrives in his paper also at these results though in a different way, namely geometrically, whilst I have worked algebraically. Mr. BROUWER arrives at a *decomposition* ("Zerlegung") of the fourdimensional rotation into two three-dimensional ones, whilst I use the expression *coordination* ("Zuordnung").

Berlin, March 28<sup>th</sup>, 1904.

**Mathematics.** — "*Algebraic deduction of the decomposability of the continuous motion about a fixed point of  $S_4$  into those of two  $S_3$ 's*". By MR. L. E. J. BROUWER. (Communicated by Prof. KORTEWEG).

As the position of  $S_4$  is determined with respect to a fixed system of axes by *six* independent variables and that of  $S_3$  with respect to a fixed system of axes by *three* independent variables we understand at once that in an infinite number of ways two  $S_3$  motions can be *coordinated* to an  $S_4$  motion, so that position and velocities of  $S_4$  are determined by position and velocities of the two  $S_3$ 's. On such a coordination Mr. JAHNKE has been engaged in the papers mentioned above and has deduced the relations between positions and velocities of  $S_4$  and the two  $S_3$ 's. Interpreted geometrically his coordination amounts to the following: Let us suppose in  $S_4$  a fixed system of axes  $X_1 X_2 X_3 X_4$ , and a movable one  $Y_1 Y_2 Y_3 Y_4$ ; let us consider the part equiangular to the right of the double rotation, which transfers  $X_1 X_2 X_3 X_4$  into  $Y_1 Y_2 Y_3 Y_4$ ; let us add to it an equal equiangular double rotation to the left (namely equal with respect to the system of axes  $X_1 X_2 X_3 X_4$ ; only with respect to a definite system of axes can we call an equiangular double rotation to the right and one to the left equal); the resulting rotation becomes a single

rotation parallel to the space  $X_1 X_2 X_3$  which would transfer the system of axes  $X_1 X_2 X_3$  into another  $Z_1 Z_2 Z_3$ . Thus to each position  $Y$  with respect to  $X_1 X_2 X_3$  answers a position  $Z$  with respect to  $X_1 X_2 X_3$ , and by interchanging right and left, in an analogous manner a position  $U$  with respect to  $X_1 X_2 X_3$ ; and we may consider the positions  $Z$  and  $U$  as coordinated to the position  $Y$ .

Not immediately to be seen are the two following properties of the  $S_4$  motion geometrically deduced in what was communicated in the February meeting.

1<sup>st</sup>. The continuous motion of  $S_4$  can be *decomposed*, that is: independent of the choice of a system of axes two definite threefoldly infinite motion groups exist in  $S_4$  in such a way that an arbitrary motion can be composed out of two motions each of which belongs to one of the groups mentioned.

2<sup>nd</sup>. The continuous motion of  $S_4$  can be *decomposed into two  $S_3$  motions*, that is, two twodimensional manifoldnesses (namely those of the systems of planes equiangular to the right and to the left) exist in  $S_4$  in such a way that each of the motion groups mentioned transforms the elements of one of them into each other and leaves the other unchanged; to which furthermore we can allow twodimensional Euclidean stars to answer in such a way that to congruent combinations in one of the manifoldnesses congruent combinations of the Euclidean stars correspond, that to the corresponding motion group of  $S_4$  answers the motion group of the Euclidean star movable as a solid and that to congruent combinations in the motion group of  $S_4$  answer congruent combinations in the motion group of the Euclidean star movable as a solid: reason why we may call the two twodimensional manifoldnesses *twodimensional Euclidean stars* and the motion groups of  $S_4$  transforming them *Euclidean threedimensional motion groups about a fixed point*.

We shall now see how we can arrive algebraically at both results.

Mr. JAHNKE takes from CASPARY the so called "Elementary transformation" (see a.o. Jahresbericht der Deutschen Mathematiker-Vereinigung XI, 4, 1902, p. 180 and F. CASPARY, *Zur Theorie der Thêtafunctionen mit zwei Argumenten*, CRELLE'S Journal, vol. 94, page 75), which has the property that an arbitrary congruent transformation of  $S_4$  can be replaced by two successive elementary transformations. The name "Elementary rotation" (Elementardrehung) of Mr. JAHNKE seems to me less fortunate, because it is a symmetric transformation, not a rotation. The real meaning of the "Elementary transformation" will be made clear furtheron. For the present we remind the readers of its determinant type (see Jahresbericht, l. c., page 180).

$$\left. \begin{array}{cccc} \alpha_1 & -\alpha_2 & \alpha_3 & \alpha_4 \\ \alpha_2 & \alpha_1 & -\alpha_4 & \alpha_3 \\ -\alpha_3 & \alpha_4 & \alpha_1 & \alpha_2 \\ \alpha_4 & \alpha_3 & \alpha_2 & -\alpha_1 \end{array} \right\} , . . . . . (I)$$

and we notice that it *does not represent a group and does not possess any three-dimensional properties* (it *does* after composition with itself, compare for instance the theorem of Mr. ЯАНКЕ, Jahresbericht, l. c., page 182 : “Jede endliche Drehung im  $R_3$  lässt sich als eine Zusammensetzung aus einer Elementardrehung im  $R_4$  mit sich selbst auffassen”<sup>1)</sup>); which operation is for the rest bound to a once chosen system of axes).

We shall now deduce two different determinant types likewise determined by a system of cosines of direction  $\alpha_1, \alpha_2, \alpha_3, \alpha_4$  which *do represent a group and have three-dimensional properties*. Those will be the determinants of equiangular double rotation to the right and to the left.

Let us solve the  $a$ 's out of the equations (H) (see Proceedings of March 19<sup>th</sup>, 1904, page 721); then we have

$$\left. \begin{array}{l} a_1 = \alpha_4 \beta_1 + \alpha_3 \beta_2 - \alpha_2 \beta_3 + \alpha_1 \beta_4 \\ a_2 = \alpha_1 \beta_2 - \alpha_3 \beta_1 + \alpha_2 \beta_4 + \alpha_4 \beta_3 \\ a_3 = \alpha_4 \beta_3 + \alpha_3 \beta_4 + \alpha_2 \beta_1 - \alpha_1 \beta_2 \\ a_4 = \alpha_4 \beta_4 - \alpha_3 \beta_3 - \alpha_2 \beta_2 - \alpha_1 \beta_1 \end{array} \right\} . . . . . (a).$$

Thus the determinant type of the equiangular double rotation to the right is

$$\left. \begin{array}{cccc} \alpha_4 & \alpha_3 & -\alpha_2 & \alpha_1 \\ -\alpha_3 & \alpha_4 & \alpha_1 & \alpha_2 \\ \alpha_2 & -\alpha_1 & \alpha_4 & \alpha_3 \\ -\alpha_1 & -\alpha_2 & -\alpha_3 & \alpha_4 \end{array} \right\} . . . . . (II)$$

Directly can be verified that this determinant type forms a group.

Likewise we deduce for the equiangular double rotation to the left  $(\alpha_1 \alpha_2 \alpha_3 \alpha_4)$ , transferring the vector  $(a_1 a_2 a_3 a_4)$  into  $(\beta_1 \beta_2 \beta_3 \beta_4)$ , the relations :

$$\left. \begin{array}{l} a_1 = -\alpha_4 \beta_1 - \alpha_3 \beta_2 + \alpha_2 \beta_3 + \alpha_1 \beta_4 \\ a_2 = \alpha_3 \beta_1 - \alpha_4 \beta_2 - \alpha_1 \beta_3 + \alpha_2 \beta_4 \\ a_3 = -\alpha_2 \beta_1 + \alpha_1 \beta_2 - \alpha_3 \beta_3 + \alpha_4 \beta_4 \\ a_4 = -\alpha_1 \beta_1 - \alpha_2 \beta_2 - \alpha_3 \beta_3 - \alpha_4 \beta_4 \end{array} \right\} . . . . . (b)$$

<sup>1)</sup> “Each finite rotation in  $S_3$  can be regarded as a composition of an elementary rotation in  $S_4$  with itself.”

from which ensues the determinant type for equiangular double rotation to the left:

$$\left. \begin{array}{cccc} -\alpha_1 & -\alpha_1 & \alpha_2 & \alpha_1 \\ \alpha_2 & -\alpha_1 & -\alpha_1 & \alpha_2 \\ -\alpha_2 & \alpha_1 & -\alpha_1 & \alpha_3 \\ -\alpha_1 & -\alpha_2 & -\alpha_3 & -\alpha_1 \end{array} \right\}, \dots \dots \dots \text{(III)}$$

and for this too the property of a group can be verified.

If we call (I') the determinant type formed by interchange of the rows and columns of (I), we can remark:

If we reverse the signs in the bottom row of type (II) type (I') appears.

If we reverse the signs in the last column of type (III) type (I') appears.

If we ask ourselves whether each arbitrary congruent transformation can be replaced by the succession of a transformation (III) and a transformation (II) the answer must be affirmative; for we shall have but to take those transformations (III) and (II) belonging to the transformations (I') which when successively applied transfer the given initial position into the given final one. (For those two ways only the intermediate positions will differ in as far as they will be each other's reflection with regard to their  $X_4$ -axis.)

This is the algebraic proof of 1°.

At the same time it has become evident that the meaning of the type (I') is an arbitrary equiangular double rotation to the right preceded by a reflection according to the  $X_4$ -axis (that is the  $X_4$ -axis of the initial position) or an arbitrary equiangular double rotation to the left followed by a reflection according to the  $X_4$ -axis (that is the  $X_4$ -axis of the final position), and that the meaning of the type (I) is an arbitrary equiangular double rotation to the right followed by a reflection according to the  $X_4$ -axis or an arbitrary equiangular double rotation to the left preceded by a reflection according to the  $X_4$ -axis.

Thus according to a preceding communication made in this meeting of the Academy (see page 785) it has been proved that the types (I) and (I') represent the most general symmetric transformation of  $S_4$ , of which the determinant type has been simplified only by particular choice of the system of coordinates.

We shall now give a proof for 2°.

Out of the relations (a) for equiangular double rotation to the

right we deduce, representing for shortness' sake  $\alpha'_2 \alpha''_3 - \alpha'_3 \alpha''_2$  etc. by  $\xi_{23}$  etc;  $\beta'_2 \beta''_3 - \beta'_3 \beta''_2$  etc. by  $\chi_{23}$  etc.:

$$\xi_{23} = (\alpha_1^2 + \alpha_4^2)\chi_{23} + (\alpha_1\alpha_2 + \alpha_3\alpha_4)\chi_{31} + (\alpha_3\alpha_1 - \alpha_2\alpha_4)\chi_{12} - (\alpha_2^2 + \alpha_3^2)\chi_{14} + \\ + (\alpha_1\alpha_2 + \alpha_3\alpha_4)\chi_{24} + (\alpha_3\alpha_1 - \alpha_2\alpha_4)\chi_{34}$$

$$\xi_{31} = (\alpha_1\alpha_2 - \alpha_3\alpha_4)(\chi_{23} + \chi_{14}) + (\alpha_2^2 + \alpha_4^2)\chi_{31} - (\alpha_3^2 + \alpha_1^2)\chi_{24} + \\ + (\alpha_2\alpha_3 + \alpha_1\alpha_4)(\chi_{12} + \chi_{34})$$

$$\xi_{12} = (\alpha_3\alpha_1 + \alpha_2\alpha_4)(\chi_{23} + \chi_{14}) + (\alpha_2\alpha_3 - \alpha_1\alpha_4)(\chi_{31} + \chi_{24}) + \\ + (\alpha_3^2 + \alpha_4^2)\chi_{12} - (\alpha_1^2 + \alpha_2^2)\chi_{34}$$

$$\chi_{14} = -(\alpha_2^2 + \alpha_4^2)\chi_{23} + (\alpha_1^2 + \alpha_3^2)\chi_{14} + (\alpha_1\alpha_2 + \alpha_3\alpha_4)(\chi_{31} + \chi_{24}) + \\ + (\alpha_3\alpha_1 - \alpha_2\alpha_4)(\chi_{12} + \chi_{34})$$

$$\chi_{24} = (\alpha_1\alpha_2 - \alpha_3\alpha_4)(\chi_{23} + \chi_{14}) - (\alpha_3^2 + \alpha_1^2)\chi_{31} + (\alpha_2^2 + \alpha_4^2)\chi_{24} + \\ + (\alpha_2\alpha_3 + \alpha_1\alpha_4)(\chi_{12} + \chi_{34})$$

$$\xi_{34} = (\alpha_3\alpha_1 + \alpha_2\alpha_4)(\chi_{23} + \chi_{14}) + (\alpha_2\alpha_3 - \alpha_1\alpha_4)(\chi_{31} + \chi_{24}) - \\ - (\alpha_1^2 + \alpha_2^2)\chi_{12} + (\alpha_3^2 + \alpha_4^2)\chi_{34}$$

from which ensues:

$$\xi_{23} + \xi_{14} = (\alpha_1^2 + \alpha_4^2 - \alpha_2^2 - \alpha_3^2)(\chi_{23} + \chi_{14}) + 2(\alpha_1\alpha_2 + \alpha_3\alpha_4)(\chi_{31} + \chi_{24}) + \\ + 2(\alpha_3\alpha_1 - \alpha_2\alpha_4)(\chi_{12} + \chi_{34})$$

$$\xi_{31} + \xi_{24} = 2(\alpha_1\alpha_2 - \alpha_3\alpha_4)(\chi_{23} + \chi_{14}) + (\alpha_2^2 + \alpha_4^2 - \alpha_3^2 - \alpha_1^2)(\chi_{31} + \chi_{24}) + \\ + 2(\alpha_2\alpha_3 + \alpha_1\alpha_4)(\chi_{12} + \chi_{34})$$

$$\xi_{12} + \xi_{34} = 2(\alpha_3\alpha_1 + \alpha_2\alpha_4)(\chi_{23} + \chi_{14}) + 2(\alpha_2\alpha_3 - \alpha_1\alpha_4)(\chi_{31} + \chi_{24}) + \\ + (\alpha_3^2 + \alpha_4^2 - \alpha_1^2 - \alpha_2^2)(\chi_{12} + \chi_{34})$$

$$\xi_{23} - \xi_{14} = \chi_{23} - \chi_{14}$$

$$\xi_{31} - \xi_{24} = \chi_{31} - \chi_{24}$$

$$\xi_{12} - \xi_{34} = \chi_{12} - \chi_{34}$$

So also if we call  $\lambda_{23}$  etc. the coefficients of position of a plane *before* the equiangular double rotation to the right and  $\mu_{23}$  etc. the coefficients of position after it:

$$\lambda_{23} + \lambda_{14} = (\alpha_1^2 + \alpha_4^2 - \alpha_2^2 - \alpha_3^2)(\mu_{23} + \mu_{14}) + 2(\alpha_1\alpha_2 + \alpha_3\alpha_4)(\mu_{31} + \mu_{24}) + \\ + 2(\alpha_3\alpha_1 - \alpha_2\alpha_4)(\mu_{12} + \mu_{34})$$

$$\lambda_{31} + \lambda_{24} = 2(\alpha_1\alpha_2 - \alpha_3\alpha_4)(\mu_{23} + \mu_{14}) + (\alpha_2^2 + \alpha_4^2 - \alpha_3^2 - \alpha_1^2)(\mu_{31} + \mu_{24}) + \\ + 2(\alpha_2\alpha_3 + \alpha_1\alpha_4)(\mu_{12} + \mu_{34})$$

$$\lambda_{12} + \lambda_{34} = 2(\alpha_3\alpha_1 + \alpha_2\alpha_4)(\mu_{23} + \mu_{14}) + 2(\alpha_2\alpha_3 - \alpha_1\alpha_4)(\mu_{31} + \mu_{24}) + \\ + (\alpha_3^2 + \alpha_4^2 - \alpha_1^2 - \alpha_2^2)(\mu_{12} + \mu_{34})$$

$$\lambda_{23} - \lambda_{14} = \mu_{23} - \mu_{14}$$

$$\lambda_{31} - \lambda_{24} = \mu_{31} - \mu_{24}$$

$$\lambda_{12} - \lambda_{34} = \mu_{12} - \mu_{34}$$

In an analogous way we deduce from the relations (b) for an equiangular double rotation to the left the following relations between the coefficients of position of a plane before and after the rotation:

$$\begin{aligned} \lambda_{23} + \lambda_{14} &= \mu_{23} + \mu_{14} \\ \lambda_{31} + \lambda_{24} &= \mu_{31} + \mu_{24} \\ \lambda_{12} + \lambda_{34} &= \mu_{12} + \mu_{34} \end{aligned}$$

$$\lambda_{23} - \lambda_{14} = (\alpha_1^2 + \alpha_4^2 - \alpha_2^2 - \alpha_3^2)(\mu_{23} - \mu_{14}) + 2(\alpha_1\alpha_2 + \alpha_3\alpha_4)(\mu_{31} - \mu_{24}) + 2(\alpha_3\alpha_1 - \alpha_2\alpha_4)(\mu_{12} - \mu_{34})$$

$$\lambda_{31} - \lambda_{24} = 2(\alpha_1\alpha_2 - \alpha_3\alpha_4)(\mu_{23} - \mu_{14}) + (\alpha_2^2 + \alpha_4^2 - \alpha_3^2 - \alpha_1^2)(\mu_{31} - \mu_{24}) + 2(\alpha_2\alpha_3 + \alpha_1\alpha_4)(\mu_{12} - \mu_{34})$$

$$\lambda_{12} - \lambda_{34} = 2(\alpha_3\alpha_1 + \alpha_2\alpha_4)(\mu_{23} - \mu_{14}) + 2(\alpha_2\alpha_3 - \alpha_1\alpha_4)(\mu_{31} - \mu_{24}) + (\alpha_3^2 + \alpha_4^2 - \alpha_1^2 - \alpha_2^2)(\mu_{12} - \mu_{34})$$

As now  $\Sigma (\lambda_{23} + \lambda_{14})^2 = 1$  and  $\Sigma (\lambda_{23} - \lambda_{14})^2 = 1$  and the determinant

$$\left. \begin{array}{ccc} \alpha_1^2 + \alpha_4^2 - \alpha_2^2 - \alpha_3^2 & 2(\alpha_1\alpha_2 + \alpha_3\alpha_4) & 2(\alpha_3\alpha_1 - \alpha_2\alpha_4) \\ 2(\alpha_1\alpha_2 - \alpha_3\alpha_4) & \alpha_2^2 + \alpha_4^2 - \alpha_3^2 - \alpha_1^2 & 2(\alpha_2\alpha_3 + \alpha_1\alpha_4) \\ 2(\alpha_3\alpha_1 + \alpha_2\alpha_4) & 2(\alpha_2\alpha_3 - \alpha_1\alpha_4) & \alpha_3^2 + \alpha_4^2 - \alpha_1^2 - \alpha_2^2 \end{array} \right\} \quad (IV)$$

represents the general congruent threedimensional transformation about a fixed point expressed in the four parameters of homogeneity, we can regard the motion group with the determinant type (II) as a congruent motion group of the twodimensional Euclidean star of the  $(\lambda_{bc} + \lambda_{a4})$ 's and the motion group with the determinant type (III) as a congruent motion group of the twodimensional Euclidean star of the  $(\lambda_{bc} - \lambda_{a4})$ 's; namely according to the determinant type (IV) about an axis with cosines of direction

$$\frac{\alpha_1}{\sqrt{1-\alpha_4^2}}, \frac{\alpha_2}{\sqrt{1-\alpha_4^2}}, \frac{\alpha_3}{\sqrt{1-\alpha_4^2}}$$

over an angle equal to  $2 \text{ arc cos } \alpha_4$ .

Let us call the  $S_r$  of the  $(\lambda_{bc} + \lambda_{a4})$ 's "the representing space to the right" or the  $S_l$  of  $S_4$  and the  $S_s$  of the  $(\lambda_{bc} - \lambda_{a4})$ 's the "representing space to the left" of the  $S_l$  of  $S_4$ , then we find that to two equiangular double rotations to the right (left)  $(\alpha_1' \alpha_2' \alpha_3' \alpha_4')$  and  $(\alpha_1'' \alpha_2'' \alpha_3'' \alpha_4'')$  of  $S_4$  whose angles of rotation are  $\text{arc cos } \alpha_4'$  and  $\text{arc cos } \alpha_4''$  and whose systems of planes of rotation make an angle with each other equal to

$$\text{arc cos } \frac{\alpha_1' \alpha_1'' + \alpha_2' \alpha_2'' + \alpha_3' \alpha_3''}{\sqrt{1-\alpha_4'^2} \cdot \sqrt{1-\alpha_4''^2}} \quad (\text{see Proceedings, March, 1904, page 724})$$

correspond two rotations of  $S_r$  ( $S_l$ ) over angles  $2 \text{ arc cos } \alpha_4'$  and  $2 \text{ arc cos } \alpha_4''$ ,

whose axes make an angle equal to  $\text{arc cos } \frac{\alpha_1' \alpha_1'' + \alpha_2' \alpha_2'' + \alpha_3' \alpha_3''}{\sqrt{1-\alpha_4'^2} \cdot \sqrt{1-\alpha_4''^2}}$

with each other. So to congruent combinations in the group of the equiangular double rotations to the right (left) in  $S_4$  correspond congruent combinations in the motion group of  $S_r(S_l)$ . As moreover the

$$\lambda_{23} + \lambda_{14}$$

$$\lambda_{31} + \lambda_{24}$$

$$\lambda_{12} + \lambda_{34}$$

of a plane are the cosines of direction of the representant of the system equiangular to the right with that plane with respect to the system of axes  $OX_r Y_r Z_r$  (defined Proceedings March 1904, p. 728), and likewise

$$\lambda_{23} - \lambda_{14}$$

$$\lambda_{31} - \lambda_{24}$$

$$\lambda_{12} - \lambda_{34}$$

the cosines of direction of the representant of the system equiangular to the left with that plane with respect to the system of axes  $OX_l Y_l Z_l$  (defined in the same place) the  $S_r$  and  $S_l$  introduced just now prove to be identical with those introduced here formerly (see Proceedings March, 1904, p. 725) so that they represent not only by their motions the equiangular motion groups of  $S_4$  to the right and to the left, but also by their vectors the systems of planes equiangular to the right and to the left (with direction of rotation) of  $S_4$  and so that the angle of the representing vectors is the angle of the systems of planes themselves.

So also to congruent combinations in the twodimensional manifoldness formed by the equiangular systems of planes to the right (left) correspond congruent combinations in  $S_r(S_l)$ . This is an algebraic proof for 2<sup>nd</sup>. to its full extent.

This deduction has at the same time made clear the meaning of the four parameters of homogeneity for the general congruent three-dimensional transformation about a fixed point, namely the cosines of direction of the vector indicating the corresponding equiangular double rotation to the right (left) of an  $S_4$  of which this  $S_3$  is the  $S_r(S_l)$  and the system of axes in  $S_3$  the system  $OX_r Y_r Z_r$  ( $OX_l Y_l Z_l$ ).

**Zoology.** — *“On the relationship of various invertebrate phyla.”*

By Prof. A. A. W. HUBRECHT.

In an elaborate paper entitled “Beiträge zu einer Trophocöltheorie,” published in 1903 in the 38th volume of the “Jenaische Zeitschrift für Naturwissenschaft,” Prof. ARNOLD LANG of Zürich (p. 68—77) gives a clear exposition of what has been, in his opinion, the phylogensis of the Annelids.

In this pedigree he places, beginning with a protocoelenterate, a ctenophore-like being, a plathelminth, an intermediate form resembling a trielade, an animal in the shape of a leech which already possesses metameric segmentation and finally a proto-annelid.

The grounds on which he bases this phylogensis, compel us to acknowledge important relations between these animal groups. But whether this kinship testifies to a descent in the order given by Lang, or whether the order has for the greater part been a reversed one, deserves to be examined more closely.

In my opinion there Ctenophores should not be placed at the beginning of the series, nor are they to be considered as links between Coelenterates and worms, but they have to be looked upon as animals, which form the last offshoots of an evolutionary series, leading from the Annelids via the Hirudinia and the Plathelminthes. Of these latter there have been some which gradually assumed a pelagic mode of life and have become Ctenophora, the external resemblance of which with transparent jelly-fish seemed to justify their being placed by the side of the Coelenterates.

Let us first test the grounds on which that combination has until now been defended (see e. g. G. C. BOURNE in RAY LANKESTER'S Treatise on Zoology, 1900).

The presence of a gastro-vascular system and the absence of an independent coelom, as well as the presence of a subepithelial nerveplexus are characteristics which can be found not only with the Coelenterates, but also to a great extent with the Plathelminths.

The tentacles of the Ctenophores have quite wrongly been compared to those of the medusae, while the analogy of the adhesive cells of the Ctenophora with the nematocysts of the Cnidaria is also defective. And if nematocysts should be found in some Ctenophora, no conclusions should be based on this, because they also occur in Molluses, Plathelminths and Nemertines.

The absence of nephridia, the general structural proportions and the gelatinous composition of part of the organism are details which

by no means interfere with a view which would see in the Ctenophora Plathelminths that have become pelagic.

That the connection which HAECKEL intended to establish between Coelenterates and Ctenophora, when describing *Ctenaria ctenophora*, is an imaginary one, has already repeatedly been shown, so e. g. by R. HERTWIG ("Jen. Zeitschr". Bd. 14, p. 444), G. C. BOURNE (l. c. p. 445) and others. The first-mentioned author says emphatically (l. c. p. 445): "Die Ctenophoren sind Organismen welche sich von den übrigen Coelenteraten sehr weit entfernen." Also KORSCHÉLT and HEIDER in their excellent handbook on the embryology of the invertebrates are inclined (p. 100) to look upon the Ctenophora rather as an independent branch of the animal kingdom, the connection of which with that of the Coelenterates lies far backward. On the other hand they point out unmistakable relations between the phylogenesis of the Ctenophora and that of the Bilateria (Annelids, Arthropoda, Molluscs etc.). They expressly add that the side-branch of the animal kingdom on which the Ctenophora are placed *cannot be considered as having furnished a starting-point for higher animal forms.*

Ctenoplana and Coeloplana are consequently not considered by them as advancing steps of development in the direction of the Plathelminths, but as aberrant, creeping Ctenophora. LANG himself has acknowledged on page 72 of his great handbook that the place of the Ctenophora among the other Cnidaria is a very problematical one and that their embryology distinguishes them from all Cnidaria.

So there can be no doubt, considering all this, that the tie which nowadays keeps together the Ctenophora with the Coelenterates has of late years been considerably slackened. One effort and it may be entirely removed<sup>1)</sup>.

What on the other hand have we to think about possible relations between Ctenophora and Plathelminths? These relations appear especially striking to those who have occupied themselves with the embryological development of both classes.

Thus SELENKA has already in 1881 summarized this analogy under twelve heads (zur Entwicklungsgeschichte der Seeplanarien, S. 283). Also LANG in his monograph on Polyclads (1884) has emphatically pleaded for that relationship, although in a separate paragraph he acknowledges the existence of real difficulties. Also in his most recent paper he adheres to the same opinion.

The discovery of two very peculiar genera of animals has still more

<sup>1)</sup> A paper, published very recently in the Zoologische Anzeiger (Bd. 27, p. 223) on a new, much simplified Ctenophore, does not, as its author DAWYDOFF suggests, strengthen the bond between Coelenterates and Ctenophora.

emphasized the problem of the relationship between Ctenophora and Plathelminths, I mean Ctenoplana and Coeloplana. In different degree they unite properties of both classes as has already been clearly elucidated by their discoverers: KOROTNEFF and KOWALEWSKY. Yet neither BOURNE who prepared the Ctenophora for RAY LANKESTER'S large Textbook of Zoology, nor KORSCHULT and HEIDER in their handbook mentioned above, nor WILLEY, who lately studied Ctenoplana in a living condition, are really convinced of the possibility of a derivation of Plathelminths from Ctenophores, in which case these two genera should have to be considered as intermediate forms in that direction.

So WILLEY e.g. points out that it is not very probable that littoral forms would have sprung from pelagic ones, whereas generally the contrary is observed. This would according to him have been a reversion of the natural sequence. The future will show, in my opinion, that the difficulties mentioned, and raised by such able experts, will for the greater part vanish as soon as relationships "against the grain", i. e. in the unnatural order, are no longer accepted, but when both genera are considered as gradually mutating Plathelminths which are already fairly on the way of assuming ctenophoran habitus.

From what precedes we may at any rate infer that whereas the Coelenterate relationship of the Ctenophora has faded, their comparability with the Plathelminths has come to the fore.

The data for judging in how far a derivation of the Annelids from Plathelminths might be possible are given in extenso especially in LANG'S earlier and later publications, more particularly in his well known Gundapaper (1881) of which he has given an improved and partly modified edition in his most recent essay, quoted in the beginning. So I need only refer to this latest paper here.

I for my part must now try to show that a derivation *in the opposite direction* presents no difficulties. We then should look upon Plathelminths and Ctenophores no longer as ancestral forms but as modified and in many respects unilaterally modified descendants of a more primitive, Annelid-like type.

LANG has already in his Polyclad-monograph (p. 674) openly declared himself against such a view. Yet in the twenty years which have since elapsed, various considerations have changed and it seems that CALDWELL'S view (Proc. R. Soc. 1882 no. 222) has become more probable again, according to which "there is a presumption . . . that in fact Platyelminths are degenerate Enterocoeles."

I should be willing like to undertake the defence of this thesis and to see in the Plathelminths degenerate forms in which the

coelom has almost entirely disappeared, while the genital apparatus has obtained a maximum degree of complication.

At the outset it seems to me to be less probable that at the base of the pedigree of the Annelids such animals should stand like the hermaphrodite Plathelminths with their ovaries, testes, vitellaria, so greatly varying in size and shape; with their shell-glands, ootype, cirrus, penes, uterus, spermatheca, etc., not even to mention the vitello-intestinal, the Laurer- and other canals. Does not this very complication force us to place such animal forms rather in the peripheral branches than near the root of any pedigree?

On the other hand we can state that in those Polychaeta which have retained archaic characters, such as *Polygordius*, *Protodrilus* and *Saccocirrus*, various peculiarities draw our attention which in Plathelminths are further developed. So the phylogenesis of the Plathelminths would not necessarily have to be so long, via Polychaeta, Oligochaeta, Hirudinea, but the type of Plathelminths might already at an early period have been a deviation of the original coelomatous ancestral forms, while in the course of this evolutionary process also the present Oligochaeta and Hirudinea might have sprung off laterally.

Meanwhile the strongest argument for the degeneration of the Plathelminths seems to me to be found in their early ontogenesis.

When we consider this in the light which not long ago especially American workers have procured to us, we ought to pay attention to the phenomena of *cell-lineage*: the descent of special groups of tissue from certain mothercells. WILSON, CONKLIN, MEAD and others have shown us the way here.

Of paramount importance is the fact that Annelids (Polychaeta Oligochaeta, Hirudinea) and Molluscs in those earliest phases of development show a striking uniformity and that e.g. in all of them the couple of mothercells of the so-called mesoblast-bands, within which the coelom and metamerism appear first, originate in a similar manner from one cell, the oldest, unpaired, mesodermic mother-cell, belonging to the 64-cellular cleavage phase.

This cell lies in the second quartet of cells reckoned from the vegetative pole and is produced by a plane of division slanting to the left. The next cleavage always divides this cell into a right and left mesodermic cell; these two develop into the paired mesodermic bands.

All this is always observed in the animal phyla above-mentioned. Concerning the Plathelminths LANG provided us already twenty years ago with extensive data, which however do not constitute an unbroken series such as is necessary for establishing the cell-lineage. Such a series was given us a few years ago (1898) for *Leptoplana*

by E. B. WILSON (Annals of the New-York Academy of Sciences, vol. XI p. 13). From his publication we may conclude as follows:

1. That a cell-couple as represented by LANG for Discocoelis, is also present in Leptoplana, which MEAD has compared to the mother-cells of the mesoblastbands of Annelids and Molluses, *although from this cell-couple no mesoblast develops in either genus of Plathelminths.*

2. That, moreover, with Leptoplana, four cells of the second cell-quartet (counted from above) become the mother-cells of "larval mesenchym", that they remove to the interior and that by further subdivision they gradually furnish the whole mesoblast of Leptoplana. This origin of the mesoblast in Plathelminths was also already known to LANG.

3. That also with Molluses (Unio, Crepidula) and probably also with certain Annelids (Aricia), beside the two symmetrical mesoblast bands still another source of mesoblastic tissue occurs, which is directly comparable to the source of larval mesenchym mentioned in 2, and that also these mesenchym mother-cells originate from cells belonging to the ectoblast quartet, as with the Plathelminths.

4. That consequently it may be considered a settled fact that with Annelids and Molluses the mesoblast has a twofold origin<sup>1)</sup>.

CONKLIN (Vol. XIII, Journal of Morphology, p. 151) has emphasized that thus mesoblast is furnished by each of the four quadrants, viz. the mesenchym by the micromeres of the second quartet of *A*, *B*, and *C*, the mesoderm-bands by *D*.

This latter phenomenon is always connected with lengthening of the body and with teloblastic growth, even with animals like Lamelibranchia and Gastropoda, although the latter are not generally looked upon as longitudinally developed forms. From this CONKLIN justly inferred that the radial mesoblast has a still more primitive character than the bilateral.

Whoever considers more closely the correspondence here noticed in the development of the Polyclada with that of the Annelids and Molluses, will have to acknowledge that only that solution can be satisfactory which considers the two cells, mentioned in 1, as the last remnant of the no longer fully developing mesoblast-bands with the degeneration of which the disappearance of the coelom and of a distinct metamerism has gone hand in hand.

<sup>1)</sup> I may briefly call attention to the fact that I also pleaded for a manifold origin of the mesoblast with mammals, on account of what had been found in Tarsius (Verh. Kon. Ak. v. Wet. Amsterdam, vol. VIII n<sup>o</sup>. 6 1902, p. 69) and that I concluded from it that the mesoderm is not equivalent to the two primary germ-layers, but that KLEINENBERG was right when he qualified it as a complex of originally independently developing organs.

To look upon them as potential mother-cells of those mesoblast-bands would be against all known laws of heredity, where in all other points there is so great a resemblance, also with regard to the mesenchym, between this 64-cellular stage and that of Annelids and Molluscs and where it would be entirely impossible — supposing evolution to have followed the line: Coelenterates, Ctenophora, Plathelminths — to derive the mesoblast-bands, which must anyhow lie accumulated in the cells mentioned, from these preceding ancestral forms. On the other hand it can easily be understood that these bands have gradually assumed their present form and peculiar characteristics in the long (and to us unknown) series of the ancestral forms of Annelids, Molluscs and Polychaeta, and that with these latter and still more with the Ctenophora (which have an ontogenesis so much resembling that of the Polychaeta,) the part played by these mesoblastic mother-cells has again receded to the back-ground.

We must then, especially on account of what ontogenesis has taught us, consider the Plathelminths as degenerate descendants of Coelomata and so the strobilation of the Cestoda, which are still further degenerated by parasitism, again falls within the reach of an explanation which would homologize it with the metameric structure of the Annelids.

How the gradual reduction leading from Polychaeta via Oligochaeta and Hirudinea to Plathelminths, has left its traces in all the different organs and tissues I will not develop more extensively here; I may suppose these points to be generally known.

It is obvious, after what has preceded, that we ought not to attempt to derive the metamerism of the Annelids from the pseudo-metamerism of the Turbellaria as LANG does. I prefer to accept the hypothesis formulated already in 1881 by SEDGWICK, according to which a longitudinally extended, actinia-like being, possessing wormlike free motility, formed the starting-point. Gradually cyclomerism was converted into bilateral symmetry and linear metamerism, in the same way as now already certain Actinia show a tendency to bilateral symmetry.

ED. VAN BENEDEK afterwards indicated (1894), though only in an oral address which has never been published, how SEDGWICK's view might be extended to the Chordates. In 1902 in the "Verhandelingen" of this Academy, I have tested the possibility of applying SEDGWICK's theory to the facts that are revealed to us by the development of mammals. And the facility with which the explanation of SEDGWICK can be extended both to Vertebrates and Invertebrates, is undoubtedly an argument in its favour.

LANG and HATSCHKE object that a prolonged actinialike being would

also have possessed unpaired tentacles and an unpaired gastral division in the median line. They forget that such an unpaired medial coelomic cavity is already present in *Balanoglossus* and that LANGERHANS ("Zeitschr. für wiss. Zool." Vol. 34, 1880) and GOODRICH (Q. J. Microsc. Sc. Vol. 44, 1901) have also shown the existence of an unpaired coelomic cavity in *Saccocirrus*, while cases of unpaired median sensory spots could be enumerated in Coelomata. The well-known antithesis of headsegment and pygidium as compared with the trunk in the bilaterally metameric Coelomata is an argument that goes far to meet LANG'S and HATSCHKE'S contention.

Neoformation of segments, still pretty equally distributed with the cyclomeric Coelenterates, but there also already variable, occurs with the Coelomata exclusively at the posterior end and with many of them only during embryonic life.

If we assume in accordance with E. VAN BENEDEN (see Verh. Kon. Akad. v. Wet. Amsterdam. Vol. VIII p. 69) that the stomodaeum of an actinia-like ancestral form has been the precursor of the chorda dorsalis, beside and above which the nerve-ring unites to a spinal chord, while under it a connection between the stomodaeal fissure (the chordal cavity) and the gastral diverticula (coelomic cavities) can be observed, then it follows from this that the ancestral forms of the aquatic Chordata are moved about in the water in a position different from that of the ancestral Articulates by 180°. The mouth of the Chordates would then have arisen later as a new formation, as has already repeatedly been asserted. It is an undoubted simplification of our phylogenetic speculations if we are entitled to look for this difference in orientation already in very early ancestral forms and can so avoid GEOFFROY ST. HILAIRE'S error who shifted the process of reversion to a much later stage of development.

If thus the phylogenesis is very considerably shortened, I may call attention to the fact that even with respect to the mammalian foetal envelopes, I showed in the above-mentioned publication the possibility of a similar shortening of their phylogenesis, by not admitting that these embryonic coverings have originated from those of reptiles and birds, as was done until now, but by considering them in direct connection with larval envelopes of invertebrate ancestral forms.

In the grouping of bilaterally symmetrical, coelomatic animals (resp. of such as have lost their coelom again) which has here been attempted, important phyla (Nemertea, Nematoids, Prosopygii, Chaetognatha, etc.) have been left out of consideration.

There are still too many gaps in our knowledge of their anatomy

and their development, to enable us to form a correct judgment about their exact position.

With regard to the Nematoda I want to add that to me it seems to be an error to look upon the parasitical Nematoda as descended from those which are nowadays found living freely in the sea or in fresh water or in moist soil. All these latter are far too uniform to allow us to look upon them as ancestral forms. This phylum can be better understood, when we consider the parasitical forms as the older primitive ones and on the other hand derive the free-living forms from them, as parasites which have adapted themselves secondarily to a free existence. What the origin of the parasitical Nematoda in their turn may have been remains an open question for the present.

Of what has been briefly summarised above, I hope to give a more elaborate exposition in the current number of the "Jenaische Zeitschrift für Naturwissenschaft" which is now going through the press, in which periodical also LANG's paper, which induced me to write this article, appeared. To that number I refer for further particulars.

**Zoology.** — Prof. MAX WEBER reads a paper: "*On some of the results of the Siboga-Expedition.*"

(This paper will not be published in these Proceedings).

**Anthropology.** — Prof. L. BOLK reads a paper on: "*The dispersion of the blonde and brunette type in our country.*"

(This paper will not be published in these Proceedings).

**Chemistry.** — Prof. C. A. LOBRY DE BRUYN also in the name of Dr. R. P. VAN CALCAR presents a paper on: "*Changes of concentration in and crystallisation from solutions by centrifugal power.*"

(This paper will not be published in these Proceedings).

**Chemistry.** — Prof. C. A. LOBRY DE BRUYN presents a paper of Mr. C. L. JUNGUS: "*Theoretical consideration concerning boundary reactions which decline in two or more successive phases.*"

(This paper will not be published in these Proceedings).

## C O N T E N T S.

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- ABSORPTION-COMPOUNDS which may change into chemical compounds or solutions. 368.
- ACETANILIDE (Transformation of acetophenoxime into) and its velocity. 773.
- ACETOPHENOXIME (Transformation of) into acetanilide and its velocity. 773:
- ACIDS (Action of hydrogen peroxyde on diketones 1, 2 and on  $\alpha$ -ketonic). 715.  
— (On the compounds of unsaturated ketones with). 325.
- AFRICA (Contributions to the determination of geographical positions on the West-coast of). II. 426.
- AFTER-IMAGES (On factual). 481.
- AGGREGATIONS (The representation of the continuity of the liquid and gaseous conditions on the one hand and the various solid) on the other by the entropy-volume-energy surface of GIBBS. 678.
- AIRMANOMETER (The determination of the pressure with a closed). 510.
- ALBERDA VAN EKENSTEIN (W.). Dibenzal- and benzalmethylglucosides. 452.
- ALLOYS (The course of the melting-point-line of). 21.
- Anatomy.** A. J. P. VAN DEN BROEK: "The foetal membranes and the placenta of *Phoca vitulina*." 610.
- Anthropology.** L. BOLK: "The dispersion of the blonde and brunette type in our country." 846.
- APPARATUS (Description of an) for regulating the pressure when distilling under reduced pressure. 665.  
— (Methods and) used in the Cryogenic Laboratory. VI. The methylchloride circulation. 668.
- AQUEOUS SOLUTIONS (A contribution to the knowledge of the course of the decrease of the vapour-tension for). 628.
- ASCUS-FORM (The) of *Aspergillus fumigatus* Fresenius. 312.
- ASPERGILLUS *fumigatus* Fresenius (The Ascus-form of). 312.
- Astronomy.** E. F. VAN DE SANDE BAKHUYZEN: "Investigation of the errors of the tables of the moon of HANSEN-NEWCOMB for the years 1895–1902." 370. 2<sup>nd</sup> paper. 412. 422.  
— C. SANDERS: "Contributions to the determination of geographical positions on the West-coast of Africa." II, 426.
- A TEN (A. H. W.) and H. W. BAKHUIS ROOZEBOOM. Abnormal solubilitylines in binary mixtures owing to the existence of compounds in the solution. 456.  
— The melting point-lines of the system sulphur + chlorine. 599.

- BACTERIA (On the) which are active in flax-rotting. 462.
- BAEYER'S tension theory (A quantitative research concerning). 410.
- BAKHUIS ROOZEBOOM (H. W.) presents a paper of J. J. VAN LAAR: "The course of the melting-point-line of alloys." 3rd communication. 21.
- The boiling-point-curves of the system sulphur and chlorine. 63.
  - presents a paper of Dr. A. SMITS and L. K. WOLFF: "The velocity of transformation of carbon monoxide." II. 66.
  - presents a paper of J. J. VAN LAAR: "On the possible forms of the melting point-curve for binary mixtures of isomorphous substances." 151. 2nd communication. 244.
  - presents a paper of Dr. A. SMITS: "The course of the solubility curve in the region of critical temperatures of binary mixtures." 171. 2nd communication. 484.
  - The phenomena of solidification and transformation in the systems  $\text{NH}_4\text{NO}_3$ ,  $\text{AgNO}_3$  and  $\text{KNO}_3$ ,  $\text{AgNO}_3$ . 259.
  - The system Bromine + Iodine. 331.
  - The sublimation lines of binary mixtures. 408.
  - presents a paper of J. J. VAN LAAR: "On the shape of melting point-curves for binary mixtures, when the latent heat required for the mixing is very small or = 0 in the two phases." 518.
  - presents a paper of Dr. A. SMITS: "A contribution to the knowledge of the course of the decrease of the vapour tension for aqueous solutions." 628.
  - presents a paper of Prof. EUG. DUBOIS: "Facts leading to trace out the motion and the origin of the underground water in our sea-provinces." 738.
  - and A. H. W. ATEN. Abnormal solubility lines in binary mixtures owing to the existence of compounds in the solution. 456.
  - The meltingpoint lines of the system sulphur + chlorine. 599.
- BAKHUYZEN (E. F. VAN DE SANDE). See SANDE BAKHUYZEN (E. F. VAN DE).
- BATTERY (A) of standard-thermoelements and its use for thermoelectric determinations of temperature. 642.
- BECKMANN-rearrangement (The); transformation of acetophenoxime into acetanilide and its velocity. 773.
- BEEKMAN (J. W.) and A. F. HOLLEMAN. Benzene fluoride and some of its derivations. 327.
- BEHRENS (T. H. H.). The conduct of vegetal and animal fibers towards coal-tar colours. 325.
- BEMMELEN (J. M. VAN). Absorption-compounds which may change into chemical compounds or solutions. 368.
- BEMMELEN (W. VAN). The daily field of magnetic disturbance. 313.
- BENZALMETHYLGLUCOSIDES (Dibenzal- and). 452.
- BENZENE (On the substitution of the core of). 735.
- DERIVATIVES (Crystallographic and molecular symmetry of position isomeric). 406.
  - FLUORIDE and some of its derivations. 327.
  - (The nitration of). 659.

- BENZIDINE (The transformation of). 262.
- BEIJERINCK (M. W.) and A. VAN DELDEN. On the bacteria which are active in flax-rotting. 462.
- BIERENS DE HAAN (D.) (Extract of a letter of V. WILLIOT on the work of): "Théorie, propriétés, formules de transformation et méthodes d'évaluation des intégrales définies." 226.
- BINARY MIXTURE (The  $\psi$ -surface in the neighbourhood of a) which behaves as a pure substance. 649.
- BINARY MIXTURES (The equations of state and the  $\psi$ -surface in the immediate neighbourhood of the critical state for) with a small proportion of one of the components (part 3). 59. (part 4). 115.
- (On the possible forms of the melting point-curve for) of isomorphous substances. 151. 2<sup>nd</sup> communication. 244.
  - (The course of the solubility curve in the region of critical temperatures of). 171. 2<sup>nd</sup> communication. 484.
  - (The sublimation lines of). 408.
  - (Abnormal solubility lines in) owing to the existence of compounds in the solution. 456.
  - (On the shape of meltingpoint-curves for) when the latent heat required for the mixing is very small or = 0 in the two phases. (3<sup>rd</sup> communication). 518.
  - (Isothermals of gravitation on the phenomena in the neighbourhood of the plait-point for). 593.
- BLANKSMA (J. J.). On the substitution of the core of Benzene. 735.
- BLONDINE and brunette type (The dispersion of the) in our country. 846.
- BOEKE (J.). On the development of the myocard in Teleosts. 218.
- BOILING-POINT CURVES (The) of the system sulphur and chlorine. 63.
- BOIS (H. E. J. G. DU). Hysteretic orientatic-phenomena. 597.
- BOLK (L.) presents a paper of A. J. P. VAN DEN BROEK: "The foetal membranes and the placenta of *Phoca vitulina*." 610.
- The dispersion of the blondine and brunette type in our country. 846.
- BONNEMA (J. H.). A piece of lime-stone of the Ceratopyge-zone from the Dutch diluvium. 319.
- Botany.** C. A. J. A. OUDEMANS and C. J. KONING: "On a Sclerotinia hitherto unknown and injurious to the cultivation of tobacco" (*Sclerotinia Nicotianae* Oud. et Koning). 48. Postscript. 85.
- PH. VAN HARREVELD: "On the penetration into mercury of the roots of freely floating germinating seeds." 182.
  - G. GRIJNS: "The Ascus-form of *Aspergillus fumigatus* Fresenius." 312.
  - C. A. J. A. OUDEMANS: "Exosporina *Laricis* Oud. — A new microscopic fungus occurring on the Larch and very injurious to this tree." 498.
  - E. VERSCHAFFELT: "Determination of the action of poisons on plants." 703.
- BOULDER-CLAY BEDS (Deep) of a latter glacial period in North-Holland. 340.
- BOUNDARY REACTIONS (Theoretical consideration concerning) which decline in two or more successive phases. 846.

- BRINKMAN (C. H.). The determination of the pressure with a closed airmanometer. 510.
- BROEK (A. J. P. VAN DEN). The foetal membrane and the placenta of *Phoca vitulina*. 610.
- BROMINE + Iodine (The system). 331.
- BROUWER (L. E. J.). On a decomposition of a continuous motion about a fixed point  $O$  of  $S_4$  into two continuous motions about  $O$  of  $S_3$ 's. 716. Observation of Dr. E. JAHNKE. 831.
- On symmetric transformation of  $S_4$  in connection with  $S_7$  and  $S_8$ . 785.
- Algebraic deduction of the decomposability of the continuous motion about a fixed point of  $S_4$  into those of two  $S_3$ 's. 832.
- BRUNETTE TYPE (The dispersion of the blondine and) in our country. 846.
- BRUYN (C. A. LOBRY DE). See LOBRY DE BRUYN (C. A.).
- BUYS-BALLOT medal (Extract from the Report made by the Committee for awarding the). 78.
- CALCAR (R. P. VAN) and C. A. LOBRY DE BRUYN. Changes of concentration in and crystallisation from solutions by centrifugal power. 846.
- CALIBRATION (The) of manometer and piezometer tubes. 532.
- CARBON DIOXIDE (Isothermals of mixtures of oxygen). I. The calibration of manometer and piezometer tubes. 532. II. The preparation of the mixtures and the compressibility at small densities. 541. III. The determination of isothermals between 60 and 140 atmospheres, and between  $-15^\circ$  C. and  $+60^\circ$  C. 554. IV. Isothermals of pure carbon dioxide between  $25^\circ$  C. and  $60^\circ$  C. and between 60 and 140 atmospheres. 565. V. Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide. 577. VI. Influence of gravitation on the phenomena in the neighbourhood of the plait point for binary mixtures. 593.
- (Isothermals of pure) between  $25^\circ$  C. and  $60^\circ$  C. and between 60 and 140 atmospheres. 565.
- (Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure). 577.
- CARBON MONOXIDE (The velocity of transformation of). II. 66.
- CARDINAAL (J.) presents a paper of J. VAN DE GRIEND JR.: "Rectifying curves." 208.
- CENTRIC DECOMPOSITION of polytopes. 366.
- CENTRIFUGAL POWER (Changes of concentration in and crystallisation from solutions by). 846.
- CERATOPYGE-ZONE (A piece of limestone from the) of the Dutch diluvium. 319.
- Chemistry. J. W. DITO: "The action of phosphorus on hydrazine." 1.
- J. W. COMMELIN and ERNST COHEN: "The electromotive force of the DANIELL-cells." 4.
- J. J. VAN LAAR: "The course of the melting-point-line of alloys" (3<sup>rd</sup> communication). 21.
- H. W. BAKHUIS ROOZEBOOM: "The boiling-point curves of the system sulphur and chlorine." 63.

- Chemistry.** A. SMITS and L. K. WOLFF: "The velocity of transformation of carbon monoxide." II. 66.
- C. A. LOBRY DE BRUYN and C. L. JUNGUIS: "The condition of hydrates of nickelsulphate in methylalcoholic solution." 91.
- C. A. LOBRY DE BRUYN and C. L. JUNGUIS: "The conductive power of hydrates of nickelsulphate dissolved in methylalcohol." 94.
- C. A. LOBRY DE BRUYN and L. K. WOLFF: "Do the Ions carry the solvent with them in electrolysis." 97.
- On intramolecular rearrangements. N<sup>o</sup>. 5. C. L. JUNGUIS: The mutual transformation of the two stereo-isomeric methyl-*d*-glucosides." 99. N<sup>o</sup>. 6. H. RAKEN: "The transformation of diphenylnitrosamine into *p*-nitroso-diphenylamine and its velocity." 267. N<sup>o</sup>. 7. C. A. LOBRY DE BRUYN and C. H. SLUITER: "The BECKMANN-rearrangement; transformation of acetophenoxime into acetanilide and its velocity." 773. N<sup>o</sup>. 8. C. L. JUNGUIS: "The mutual transformation of the two stereoisomeric pentacetates of *d*-glucose." 779.
- S. TYMSTRA Bz.: "The electrolytic conductivity of solutions of sodium in mixtures of ethyl or methylalcohol and water." 104.
- J. J. VAN LAAR: "On the possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances." 151. 2<sup>nd</sup> communication. 244.
- A. SMITS: "The course of the solubility curve in the region of critical temperatures of binary mixtures." 171. 2<sup>nd</sup> communication. 484.
- A. F. HOLLEMAN: "Preparation of Cyclohexanol." 201.
- H. W. BAKHUIS ROOZEBOOM: "The phenomena of solidification and transformation in the systems  $\text{NH}_4\text{NO}_3$ ,  $\text{AgNO}_3$  and  $\text{KNO}_3$ ,  $\text{AgNO}_3$ ." 259.
- A. F. HOLLEMAN and J. POTTER VAN LOON: "The transformation of benzidine." 262.
- S. HOOGEWERFF and W. A. VAN DORP: "On the compounds of unsaturated ketones with acids." 325.
- TH. H. BEHRENS: "The conduct of vegetal and animal fibers towards coal-tar-colours." 325.
- A. F. HOLLEMAN and J. W. BEEKMAN: "Benzene fluoride and some of its derivations." 327.
- H. W. BAKHUIS ROOZEBOOM: "The system Bromine + Iodine." 331.
- R. O. HERZOG: "On the action of Emulsin." 332.
- J. M. VAN BEMMELN: "Absorption-compounds which may change into chemical compounds or solutions." 368.
- F. M. JAEGER: "Crystallographic and molecular symmetry of position isomeric benzene derivatives." 406.
- H. W. BAKHUIS ROOZEBOOM: "The sublimation lines of binary mixtures." 408.
- A. F. HOLLEMAN and G. L. VOERMAN: "A quantitative research concerning BAEYERS's tension theory." 410.
- W. ALBERDA VAN EKENSTEIN: "Dibenzal- and benzalmethylglucosides." 452.
- C. H. SLUITER: "The transformation of isonitrosoacetophenonsodium into sodium benzoate and hydrogen cyanide." 453.

- Chemistry.** H. W. BAKHUIS ROOZEBOOM and A. H. W. ATEN: "Abnormal solubility lines in binary mixtures owing to the existence of compounds in the solution." 456.
- J. J. VAN LAAR: "On the shape of meltingpoint-curves for binary mixtures, when the latent heat required for the mixing is very small or = 0 in the two phases." (3<sup>rd</sup> communication). 518.
- H. W. BAKHUIS ROOZEBOOM and A. H. W. ATEN: "The meltingpoint lines of the system sulphur + chlorine." 599.
- A. W. VISSER: "Enzymactions considered as equilibria in a homogenous system." 605.
- A. SMITS: "A contribution to the knowledge of the course of the decrease of the vapour tension for aqueous solutions." 628.
- A. F. HOLLEMAN: "The nitration of Benzene fluoride." 659.
- JAN RUTTEN: "Description of an apparatus for regulating the pressure when distilling under reduced pressure." 665.
- P. VAN ROMBURGH: "On Ocimene." 700.
- P. VAN ROMBURGH: "Additive compounds of s. trinitrobenzene." 702.
- A. F. HOLLEMAN: "Action of hydrogen peroxyde on diketones 1,2 and on  $\alpha$ -ketonic acids." 715.
- C. A. LOBRY DE BRUYN and L. K. WOLFF: "Can the presence of the molecules in solutions be proved by application of the optical method of TYNDALL." 735.
- J. J. BLANKSMA: "On the substitution of the core of Benzene." 735.
- C. A. LOBRY DE BRUYN and R. P. VAN CALCAR: "Changes of concentration in and crystallisation from solutions by centrifugal power." 846.
- C. L. JUNGUIS: "Theoretical consideration concerning boundary reactions which decline in two or more successive phases." 846.
- CHLORINE** (The boiling-point curves of the system sulphur and). 63.
- (The meltingpoint lines of the system sulphur +). 599.
- CIRCLE POINTS** at infinity (The singularities of the focal curve of a plane general curve touching the line at infinity  $\sigma$  times and passing  $\epsilon$  times through each of the imaginary). 621.
- CLAUSIUS** and **VAN DER WAALS** (On the equations of) for the mean length of path and the number of collisions. 787.
- COAL-TAR-COLOURS** (The conduct of vegetal and animal fibers towards). 325.
- COHEN (ERNST)** and **J. W. COMMELIN**. The electromotive force of the DANIELL-cells. 4.
- COLLISIONS** (On the equations of CLAUSIUS and VAN DER WAALS for the mean length of path and the number of). 787.
- COMMELIN (J. W.)** and **ERNST COHEN**. The electromotive force of the DANIELL-cells. 4.
- COMPLEXES** of rays (On) in relation to a rational skew curve. 12.
- COMPONENTS** of a quadruplet (On the double refraction in a magnetic field near the). 19.
- COMPOUNDS** (On the) of unsaturated ketones with acids. 325.
- (Absorption-compounds which may change into chemical) or solutions. 368.
- (Abnormal solubility lines in binary mixtures owing to the existence of) in the solution. 456.

- COMPOUNDS (Additive) of *s*. trinitrobenzene. 702.
- COMPRESSIBILITY (The preparation of the mixtures and the) at small densities. 541.
- CONCENTRATION (Changes of) in and crystallisation from solutions by centrifugal power. 846.
- CONDUCTIVE POWER (The) of hydrates of nickelsulphate dissolved in methylalcohol. 94.
- CONDUCTIVITY (The electrolytic) of solutions of sodium in mixtures of ethyl- or methylalcohol and water. 104.
- CONICS (On systems of) belonging to involutions on rational curves. 505.
- CONTINUITY (The representation of the) of the liquid and gaseous conditions on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of GIBBS. 673.
- CONTINUOUS MOTION (On a decomposition of a) about a fixed point  $O$  of  $S_4$  into two continuous motions about  $O$  of  $S_3$ 's. 716. Observation of Dr. E. JAHNKE. 831.
- (Algebraic deduction of the decomposability of the) about a fixed point of  $S_4$  into those of two  $S_3$ 's. 832.
- COURSE (The) of the melting-point-line of alloys. 21.
- of the decrease (A contribution to the knowledge of the) of the vapour tension for aqueous solutions. 628.
- CRITICAL STATE (The equations of state and the  $\psi$ -surface in the immediate neighbourhood of the), for binary mixtures with a small proportion of one of the components (part 3). 59. (part 4). 115.
- (The equilibrium between a solid body and a fluid phase, especially in the neighbourhood of the). 230. 2<sup>nd</sup> part. 357.
- CRITICAL TEMPERATURES (The course of the solubility curve in the region of) of binary mixtures. 171. 2<sup>nd</sup> communication. 484.
- CROMMELIN (C. A.) and H. KAMERLINGH ONNES. On the measurement of very low temperatures. VI. Improvements of the protected thermoelements; a battery of standard-thermoelements and its use for thermoelectric determinations of temperature. 642.
- CRYOGENIC LABORATORY (Methods and apparatus used in the). VI. The methylchloride circulation. 668.
- CRYSTALLISATION (Changes of concentration in and) from solutions by centrifugal power. 846.
- CRYSTALLOGRAPHIC and molecular symmetry of position isomeric benzene derivatives. 406.
- CUBIC CURVE (The harmonic curves belonging to a given plane). 197.
- CURVE (The singularities of the focal curve of a plane general) touching the line at infinity  $\sigma$  times and passing  $\varepsilon$  times through each of the imaginary circle points at infinity. 621.
- in  $S_4$  (PLÜCKER's numbers of a). 501.
- CURVE IN SPACE (The singularities of the focal curve of a). 17.
- CURVES (An equation of reality for real and imaginary plane) with higher singularities. 764.
- (On systems of conics belonging to involutions on rational). 505.
- (Fundamental involutions on rational) of order five. 503.

- CURVES (The harmonic) belonging to a given plane cubic curve. 197.  
 — (Rectifying). 208.
- CYCLOHEXANOL (Preparation of). 201.
- DAILY FIELD (The) of magnetic disturbance. 313.
- DANIELL-CELLS (The electromotive force of the). 4.
- DECOMPOSABILITY (Algebraic deduction of the) of the continuous motion about a fixed point of  $S_4$  into those of two  $S_3$ 's. 832.
- DEKHUYZEN (M. C.) and P. VERMAAT. On the epithelium of the surface of the stomach. 30.
- DELLEN (A. VAN) and M. W. BEIJERINCK. On the bacteria which are active in flax-rotting. 462.
- DIBENZAL- and benzal-methylglucosides. 452.
- DIFFERENTIAL EQUATION (On the) of MONGE. 620.
- DIKETONES 1,2 (Action of hydrogenperoxyde on) and on  $\alpha$ -ketonic acids. 715.
- DILUVIUM (A piece of lime-stone of the Ceratopyge-zone from the Dutch). 319.
- DIPHENYLNITROSAMINE (The transformation of) into *p*-nitroso-diphenylamine and its velocity. 267.
- DISPERSION (The) of the blondine and brunette type in our country. 846.  
 — of light (The periodicity of solar phenomena and the corresponding periodicity in the variations of meteorological and earth-magnetic elements, explained by the). 270.
- DITO (J. W.). The action of phosphorus on hydrazine. 1.
- DORP (W. A. VAN) and S. HOOGEWERFF. On the compounds of unsaturated ketones with acids. 325.
- DUBOIS (EUG.). Deep boulder-clay beds of a latter glacial period in North-Holland. 340.  
 — Facts leading to trace out the motion and the origin of the underground water in our sea-provinces. 738.
- DIJK (G. VAN) and J. KUNST. A determination of the electrochemical equivalent of silver. 441.
- EARTH-MAGNETICAL elements (The periodicity of solar phenomena and the corresponding periodicity in the variations of meteorological and), explained by the dispersion of light. 270.
- EFFECT (A new law concerning, the relation between stimulus and) (6<sup>th</sup> communication). 73.
- EINTHOVEN (W.). The string-galvanometer and the human electrocardiogram. 107.  
 — On some applications of the string-galvanometer. 707.
- EKENSTEIN (W. ALBERDA VAN). See ALBERDA VAN EKENSTEIN (W.).
- ELECTROCARDIOGRAM (The string-galvanometer and the human). 107.
- ELECTROCHEMICAL equivalent of silver (A determination of the). 441.
- ELECTROLYSIS (Do the ions carry the solvent with them in). 97.
- ELECTROMAGNETIC phenomena in a system moving with any velocity smaller than that of light. 809.
- ELECTROMOTIVE-FORCE (The) of the DANIELL-cells. 4.
- EMULSION (On the action of). 332.

- ENTROPY-VOLUME-ENERGY SURFACE of GIBBS (The representation of the continuity of the liquid and gaseous conditions on the one hand and the various solid aggregations on the other by the). 678.
- ENZYMATIONS considered as equilibria in a homogenous system. 605.
- EPITHELIUM (On the) of the surface of the stomach. 30.
- EQUATION OF CONDITION (The liquid state and the). 123.
- EQUATION OF REALITY (An) for real and imaginary plane curves with higher singularities. 764.
- EQUATION OF STATE (On VAN DER WAALS'). 794.
- EQUATIONS (On the) of CLAUSIUS and VAN DER WAALS for the mean length of path and the number of collisions. 787.
- EQUATIONS OF STATE (The) and the  $\psi$ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components (part 3). 59. (part 4). 115.
- EQUILIBRIA (Enzymactions considered as) in a homogenous system. 605.
- EQUILIBRIUM (The) between a solid body and a fluid phase, especially in the neighbourhood of the critical state. 230. 2nd part. 357.
- ETHYL- or methylalcohol (The electrolytic conductivity of solutions of sodium in mixtures of). 104.
- EXOSPORINA LARICIS OUD. — A new microscopic fungus occurring on the Larch and very injurious to this tree. 498.
- FIBERS (The conduct of vegetal and animal) towards coal-tar-colours. 325.
- FLAX-ROTTING (On the bacteria which are active in). 462.
- FOCAL CURVE (The singularities of the) of a curve in space. 17.  
— (The singularities of the) of a plane general curve touching the line at infinity  $\sigma$  times and passing  $\varepsilon$  times through each of the imaginary circle points at infinity. 621.
- FOETAL MEMBRANE (The) and the placenta of *Phoca vitulina*. 610.
- FRANCHIMONT (A. P. N.) presents the dissertation of Dr. F. M. JAEGER: "Crystallographic and molecular symmetry of position isomeric benzene derivatives." 406.
- FUNGUS (A new microscopic) occurring on the Larch and very injurious to this tree. 498.
- GASEOUS conditions (The representation of the continuity of the liquid and) on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of GIBBS. 678.
- GEEST (J.) and P. ZEEMAN. On the double refraction in a magnetic field near the components of a quadruplet. 19.
- GEOGRAPHICAL POSITIONS (Contributions to the determination of) on the West-coast of Africa. II. 426.
- Geology. J. H. BONNEMA: "A piece of lime-stone of the Ceratopyge-zone from the Dutch diluvium." 319.  
— EUG. DUBOIS: "Deep boulder-clay beds of a latter glacial period in North-Holland." 340.

- Geology.** EUG. DUBOIS: "Facts leading to trace out the motion and the origin of the underground water in our sea-provinces." 738.
- GIBBS (The representation of the continuity of the liquid and gaseous conditions on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of). 678.
- GLACIAL PERIOD (Deep boulder-clay beds of a latter) in North-Holland. 340.
- GLUCOSE (The mutual transformation of the two stereoisomeric pentacetates of *d*-). 779.
- GLUCOSIDES (The mutual transformation of the two stereoisomeric methyl-*d*-). 99.
- GORTER (A.). The cause of sleep. 86.
- GRAVITATION (Influence of) on the phenomena in the neighbourhood of the plaitpoint for binary mixtures. 593.
- GRIEND J.R. (J. VAN DE). Rectifying curves. 208.
- GRIJNS (G.). The Ascus-form of *Aspergillus fumigatus* Fresenius. 312.
- HAGA (H.). Extract from the Report made by the committee for awarding the Buys-BALLOT medal. 78.
- presents a paper of G. VAN DIJK and J. KUNST: "A determination of the electrochemical equivalent of silver." 441.
- HAMBURGER (H. J.) presents a paper of E. HEKMA: "On the liberation of trypsin from trypsin-zymogen." 34.
- HAPPEL (H.) and H. KAMERLINGH ONNES. The representation of the continuity of the liquid and gaseous conditions on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of GIBBS. 678.
- HARREVELD (P H. VAN). On the penetration into mercury of the roots of freely floating germinating seeds. 182.
- HEKMA (E.). On the liberation of trypsin from trypsin-zymogen. 34.
- HERZOG (R. O.). On the action of Emulsin. 332.
- HOLLEMAN (A. F.). Preparation of Cyclohexanol. 201.
- The nitration of Benzene fluoride. 659.
- Action of hydrogen peroxyde on diketones 1,2 and on  $\alpha$ -ketonic acids. 715.
- and J. W. BEEKMAN. Benzene fluoride and some of its derivations. 327.
- and J. POTTER VAN LOON. The transformation of benzidine. 262.
- and G. L. VOERMAN. A quantitative research concerning BAEYER's tension theory. 410.
- HOMOGENOUS SYSTEM (Enzymactions considered as equilibria in a). 605.
- HOOGWERFF (S.) presents a paper of JAN RUITEN: "Description of an apparatus for regulating the pressure when distilling under reduced pressure." 665.
- and W. A. VAN DORP. On the compounds of unsaturated ketones with acids. 325.
- HUBRECHT (A. A. W.) presents a paper of Prof. HANS STRAHL: "The process of involution of the mucous membrane of the uterus of *Tarsius spectrum* after parturition." 302.
- On the relationship of various invertebrate phyla. 839.
- HYDRATES of nickelsulphate (The condition of) in methylalcoholic solution. 91.
- (The conductive power of) dissolved in methylalcohol. 94.
- HYDRAZINE (The action of phosphorus on). 1.

- HYDROGEN CYANIDE (The transformation of isonitrosoacetophenonsodium into sodium benzoate and). 453.
- HYDROGEN PEROXYDE (Action of) on diketones 1,2 and  $\alpha$ -ketonic acids. 715.
- HYSTERETIC orientatic-phenomena. 597.
- INTÉGRALES DÉFINIES (Extract of a letter of V. WILLIOT on the work of D. BIERENS DE HAAN : "Théorie, propriétés, formules de transformation et méthodes d'évaluation des). 226.
- INVERTEBRATE PHYLA (On the relationship of various). 839.
- INVOLUTION (The process of) of the mucous membrane of the uterus of *Tarsius spectrum* after parturition. 302.
- INVOLUTIONS (On systems of conics belonging to) on rational curves. 505.  
— (Fundamental) on rational curves of order five. 508.
- IODINE (The system Bromine +). 331.
- IONS (Do the) carry the solvent with them in electrolysis. 97.
- ISOMORPHOUS SUBSTANCES (On the possible forms of the meltingpoint-curve for binary mixtures of). 151. 2<sup>nd</sup> communication. 244.
- ISONITROSOACETOPHENONSODIUM (The transformation of) into sodium benzoate and hydrogen cyanide. 453.
- ISOTHERMALS of mixtures of oxygen and carbon dioxide. I. The calibration of manometer and piezometer tubes. 532. II. The preparation of the mixtures and the compressibility at small densities. 541. III. The determination of isothermals between 60 and 140 atmospheres, and between  $-15^{\circ}$  C. and  $+60^{\circ}$  C. 554. IV. Isothermals of pure carbon dioxide between  $25^{\circ}$  C. and  $60^{\circ}$  C. and between 60 and 140 atmospheres. 565. V. Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide. 577. VI. Influence of gravitation on the phenomena in the neighbourhood of the plaitpoint for binary mixtures. 593.
- J A E G E R (F. M.). Crystallographic and molecular symmetry of position isomeric benzene derivatives. 406.
- J A H N K E (E.). Observation on the paper of Mr. BROUWER : "On a decomposition of the continuous motion about a point  $O$  of  $S_3$  into two continuous motions about  $O$  of  $S_3$ 's. 831.
- J U L I U S (W. H.) presents a communication of J. W. COMMELIN and ERNST COHEN : "The electromotive force of the DANIELL-cells." 4.  
— Extract from the Report made by the Committee for awarding the BUYS-BALLOT medal. 78.  
— The periodicity of solar phenomena and the corresponding periodicity in the variations of meteorological and earth-magnetic elements, explained by the dispersion of light. 270.
- J U N G I U S (C. L.). The mutual transformation of the two stereo-isomeric methyl-*D*-glucosides. 99.  
— The mutual transformation of the two stereo-isomeric pentacetates of *D*-glucose. 779.

- J U N G I U S (C. L.). Theoretical consideration concerning boundary reactions which decline in two or more successive phases. 846.
- and C. A. LOBRY DE BRUYN. The condition of hydrates of nickelsulphate in methylalcoholic solution. 91.
- The conductive power of hydrates of nickelsulphate dissolved in methylalcohol. 94.
- K A M E R L I N G H O N N E S (H.) presents a paper of Dr. J. E. VERSCHAFFELT: "Contributions to the knowledge of VAN DER WAALS- $\psi$ -surface. VII. The equations of state and the  $\psi$ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components (part 3). 59. (part 4). 115. VIII. The  $\psi$ -surface in the neighbourhood of a binary mixture which behaves as a pure substance." 649.
- presents a paper of W. H. KEESOM: "Isothermals of mixtures of oxygen and carbon dioxide. I. The calibration of manometer and piezometer tubes. 532. II. The preparation of the mixtures and the compressibility at small densities. 541. III. The determination of isothermals between 60 and 140 atmospheres, and between  $-15^{\circ}$  C. and  $+60^{\circ}$  C. 554. IV. Isothermals of pure carbon dioxide between  $25^{\circ}$  C. and  $60^{\circ}$  C. and between 60 and 140 atmospheres. 565. V. Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen and the comparison of them with those of pure carbon dioxide. 577. VI. Influence of gravitation on the phenomena in the neighbourhood of the plaitpoint for binary mixtures." 593.
- Methods and apparatus used in the cryogenic laboratory. VI. The methylchloride circulation. 668.
- presents a paper of Dr. L. H. SIERTSEMA: "Investigation of a source of errors in measurements of magnetic rotations of the plane of polarisation in absorbing solutions." 760.
- and C. A. CROMMELIN. On the measurement of very low temperatures. VI. Improvements of the protected thermoelements; a battery of standard-thermoelements and its use for thermoelectric determinations of temperature. 642.
- and H. HAPPEL. The representation of the continuity of the liquid and gaseous conditions on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of GIBBS. 678.
- K A P T E Y N (W.). On the differential equation of MONGE. 620.
- K E E S O M (W. H.). Isothermals of mixtures of oxygen and carbon dioxide. I. The calibration of manometer and piezometer tubes. 532. II. The preparation of the mixtures and the compressibility at small densities. 541. III. The determination of isothermals between 60 and 140 atmospheres, and between  $-15^{\circ}$  C. and  $+60^{\circ}$  C. 554. IV. Isothermals of pure carbon dioxide between  $25^{\circ}$  C. and  $60^{\circ}$  C. and between 60 and 140 atmospheres. 565. V. Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide. 577. VI. Influence of gravitation on the phenomena in the neighbourhood of the plaitpoint for binary mixtures. 593.

- KETONES (On the compounds of unsaturated) with acids. 325.
- KLUYVER (J. C.). Series derived from the series  $\sum \frac{\rho(m)}{m}$ . 305.
- KOHNSTAMM (PH.). On the equations of CLAUSIUS and VAN DER WAALS for the mean length of path and the number of collisions. 787.
- On VAN DER WAALS' equation of state. 794.
- KONING (C. J.) and C. A. J. A. OUDEMANS. On a Sclerotinia hitherto unknown and injurious to the cultivation of tobacco, (*Sclerotinia Nicotianae* Oud. et Koning). 48. Postscript. 85.
- KORTEWEG (D. J.) presents a paper of L. E. J. BROUWER: "On a decomposition of a continuous motion about a fixed point  $O$  of  $S_4$  into two continuous motions about  $O$  of  $S_3$ 's." 716. Observation of Dr. E. JAHNKE. 831.
- presents a paper of FRED. SCHUH: "An equation of reality for real and imaginary plane curves with higher singularities." 764.
- presents a paper of L. E. J. BROUWER: "On symmetric transformation of  $S_4$  in connection with  $S_r$  and  $S_l$ ." 785.
- presents a paper of L. E. J. BROUWER: "Algebraic deduction of the decomposability of the continuous motion about a fixed point of  $S_4$  into those of two  $S_3$ 's." 832.
- KUENEN (J. P.). On the critical mixing-point of the two liquids. 387.
- KUNST (J.) and G. VAN DIJK. A determination of the electrochemical equivalent of silver. 441.
- LAAR (J. J. VAN). The course of the meltingpoint-line of alloys. (3rd communication). 21.
- On the possible forms of the meltingpoint-curve for binary mixtures of isomorphous substances. 151. 2nd communication. 244.
- On the shape of meltingpoint-curves for binary mixtures, when the latent heat required for the mixing is very small or  $= 0$  in the two phases. (3rd communication). 518.
- LATERAL AREAS (Something concerning the growth of the) of the trunkdermatomata on the caudal portion of the upper extremity. 392.
- LAW (A new) concerning the relation between stimulus and effect. (6th communication). 73.
- of distillation (Note on SYDNEY YOUNG'S). 807.
- LENGTH OF PATH (On the equations of CLAUSIUS and VAN DER WAALS for the mean) and the number of collisions. 787.
- LIGHT (Electromagnetic phenomena in a system moving with any velocity smaller than that of). 809.
- LIME-STONE (A piece of) of the Ceratopyge-zone from the Dutch diluvium. 319.
- LINE AT INFINITY (The singularities of the focal curve of the plane general curve touching the)  $\sigma$  times and passing  $\varepsilon$  times through each of the imaginary circle points at infinity. 621.

- LIQUID and gaseous conditions (The representation of the continuity of the) on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of GIBBS. 678.
- LIQUIDS (On the critical mixing-point of the' two). 387.
- LIQUID STATE (The) and the equation of condition. 123.
- LOBRY DE BRUYN (C. A.) presents a paper of J. W. DITO: "The action of phosphorus on hydrazine." 1.
- Do the Ions carry the solvent with them in electrolysis. 97.
  - presents a paper "On intramolecular rearrangements." N<sup>o</sup>. 5. C. L. JUNGUIS: "The mutual transformation of the two stereoisomeric methyl-*d*-glucosides." 99.
  - N<sup>o</sup>. 6. H. RAKEN: "The transformation of diphenylnitrosamine into *p*-nitrosodiphenylamine and its velocity." 267. N<sup>o</sup>. 7. C. A. LOBRY DE BRUYN and C. H. SLUITER: "The BECKMANN-rearrangement; transformation of acetophenoxime into acetanilide and its velocity." 773. N<sup>o</sup>. 8. C. L. JUNGUIS: "The mutual transformation of the two stereoisomeric pentacetates of *d*-glucose." 779.
  - presents a paper of S. TYMSTRA BZ.: "The electrolytic conductivity of solutions of Sodium in mixtures of ethyl- or methylalcohol and water." 104.
  - presents a paper of Dr. TH. WEEVERS and Mrs. C. J. WEEVERS-DE GRAAFF: "Investigations of some Xanthine derivatives in connection with the internal mutation of plants." 203.
  - presents a paper of W. ALBERDA VAN EKENSTEIN: "Dibenzal- and benzal-methylglucosides." 452.
  - presents a paper of C. H. SLUITER: "The transformation of isonitrosoacetophenonsodium into sodium benzoate and hydrogen cyanide." 453.
  - presents a paper of A. W. VISSER: "Enzymactions considered as equilibria in a homogenous system." 665.
  - presents a paper of Prof. P. VAN ROMBURGH: "On Ocimene." 700.
  - presents a paper of Prof. P. VAN ROMBURGH: "Additive compounds of *s*. trinitrobenzene." 702.
  - presents a paper of Prof. E. VERSCHAFFELT: "Determination of the action of poisons on plants." 703.
  - presents a paper of Dr. J. J. BLANKSMA: "On the substitution of the core of Benzene." 725.
  - presents a paper of C. L. JUNGUIS: "Theoretical consideration concerning boundary reactions which decline in two or more successive phases." 846.
  - and R. P. VAN CALCAR. Changes of concentration in and crystallisation from solutions by centrifugal power. 846.
  - and C. L. JUNGUIS. The condition of hydrates of nickelsulphate in methylalcoholic solution. 91.
  - The conductive power of hydrates of nickelsulphate dissolved in methylalcohol. 94.
  - and L. K. WOLFF. Can the presence of the molecules in solutions be proved by application of the optical method of TYNDALL? 735.
- LOON (J. POTTER VAN). See POTTER VAN LOON (J.).

LORENTZ (H. A.) presents a paper of A. PANNEKOEK: "Some remarks on the reversibility of molecular motions." 42.

— Electromagnetic phenomena in a system moving with any velocity smaller than that of light. 809.

MAGNETIC DISTURBANCE (The daily field of). 313.

MAGNETIC FIELD (On the double refraction in a) near the components of a quadruplet. 19.

MAGNETIC ROTATIONS (Investigation of a source of errors in measurements of) of the plane of polarisation in absorbing solutions. 760.

MANOMETER- and piezometertubes (The calibration of). 532.

MARTIN (K.) presents a paper of J. H. BONNEMA: "A piece of lime-stone of the Ceratopyge-zone from the Dutch diluvium." 319.

— presents a paper of Prof. EUG. DUBOIS: "Deep boulder-clay beds of a latter glacial period in North-Holland." 340.

**Mathematics.** J. DE VRIES: "On complexes of rays in relation to a rational skew curve." 12.

— W. A. VERSLUYS: "The singularities of the focal curve of a curve in space." 17.

— JAN DE VRIES: "The harmonic curves belonging to a plane cubic curve." 197.

— J. VAN DE GRIEND JR.: "Rectifying curves." 208.

— Extract of a letter of V. WILLIOT on the work of D. BIERENS DE HAAN: "Théorie, propriétés, formules de transformation et méthodes d'évaluation des intégrales définies." 226.

— J. C. KLUYVER: "Series derived from the series  $\sum \frac{\nu(m)}{m}$ ." 305.

— P. H. SCHOUTE: "Centric decomposition of polytopes." 366.

— P. H. SCHOUTE: "PLÜCKER's numbers of a curve in  $S_4$ ." 501.

— JAN DE VRIES: "On systems of conics belonging to involutions on rational curves." 505.

— JAN DE VRIES: "Fundamental involutions on rational curves of order five." 508.

— W. KAPTEYN: "On the differential equation of MONGE." 620.

— W. A. VERSLUYS: "The singularities of the focal curve of a plane general curve touching the line at infinity  $\sigma$  times and passing  $\varepsilon$  times through each of the imaginary circle points at infinity." 621.

— W. A. VERSLUYS: "On the position of the three points which a twisted curve has in common with its osculating plane." 622.

— L. E. J. BROUWER: "On a decomposition of a continuous motion about a fixed point  $O$  of  $S_4$  into two continuous motions about  $O$  of  $S_3$ 's." 716. Observation of Dr. E. JAHNKE. 831.

— FRED. SCHUH: "An equation of reality for real and imaginary plane curves with higher singularities." 764.

— P. H. SCHOUTE: "Regular projections of regular polytopes." 783.

— L. E. J. BROUWER: "On symmetric transformation of  $S_4$  in connection with  $S_r$  and  $S_t$ ." 785.

- Mathematics.** L. E. J. BROUWER: "Algebraic deduction of the decomposability of the continuous motion about a fixed point of  $S_4$  into those of two  $S_3$ 's." 832.
- MEASUREMENT** (On the) of very low temperatures. VI. Improvements of the protected thermoelements; a battery of standard-thermoelements and its use for thermoelectric determinations of temperature. 642.
- MEASUREMENTS** (Investigation of a source of errors in) of magnetic rotations of the plane of polarisation in absorbing solutions. 760.
- MELTINGPOINT-CURVE** (On the possible forms of the) for binary mixtures for isomorphous substances. 151. (2nd communication). 244.
- MELTINGPOINT-CURVES** (On the shape of) for binary mixtures, when the latent heat required for the mixing is very small or = 0 in the two phases. (3rd communication). 518.
- MELTINGPOINT-LINE** of alloys (The course of the). 21.
- MELTINGPOINT-LINES** (The) of the system sulphur + chlorine. 599.
- MERCURY** (On the penetration into) of the roots of freely floating germinating seeds. 182.
- METEOROLOGICAL** and earth-magnetical elements (The periodicity of solar phenomena and the corresponding periodicity in the variations of), explained by the dispersion of light. 270.
- Meteorology.** Extract from the Report made by the Committee for awarding the Buys-BALLOT medal. 78.
- METHODS** and apparatus used in the cryogenic Laboratory. VI. The methylchloride circulation. 668.
- METHYLALCOHOL** (The conductive power of hydrates of nickelsulphate dissolved in). 94.  
— and water (The electrolytic conductivity of solutions of sodium in mixtures of ethyl-or). 104.
- METHYLALCOHOLIC SOLUTION** (The condition of hydrates of nickelsulphate in). 91.
- METHYLCHLORIDE** circulation (The). 668.
- Microbiology.** M. W. BELJERINCK and A. VAN DELDEN: "On the bacteria which are active in flax-rotting." 462.
- MIXING POINT** (On the critical) of the two liquids. 387.
- MIXTURES** of ethyl- or methylalcohol and water (The electrolytic conductivity of solutions of sodium in). 104.  
— (The equations of state and the  $\psi$ -surface in the immediate neighbourhood of the critical state for binary) with a small proportion of one of the components. 59.  
— (Isothermals of) of oxygen and carbon dioxide. I. The calibration of manometer and piezometertubes. 532. II. The preparation of the mixtures and the compressibility at small densities. 541. III. The determination of isothermals between 60 and 140 atmospheres, and between  $-15^\circ$  C. and  $+60^\circ$  C. 554. IV. Isothermals of pure carbon dioxide between  $25^\circ$  C. and  $60^\circ$  C. and between 60 and 140 atmospheres. 565. V. Isothermals of mixtures of the molecular compositions 0.1047 and 0.1934 of oxygen, and the comparison of them with those of pure carbon dioxide. 577. VI. Influence of gravitation on the phenomena in the neighbourhood of the plaitpoint for binary mixtures. 593.

- MIXTURES (The preparation of the) and the compressibility at small densities. 541.  
 — (Isothermals of) of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide. 577.
- MOLECULAR COMPOSITIONS (Isothermals of mixtures of the) 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide. 577.
- MOLECULAR MOTIONS (Some remarks on the reversibility of). 42.
- MOLECULES (Can the presence of the) in solutions be proved by application of the optical method of TYNDALL. 735.
- MOLL (J. W.) presents a paper of PH. VAN HARBEVELD: "On the penetration into mercury of the roots of freely floating germinating seeds." 182.
- MONGE (On the differential equation of). 620.
- MOTION (Algebraic deduction of the decomposability of the continuous) about a fixed point of  $S_4$  into those of two  $S_3$ 's. 832.  
 — (Facts leading to trace out the) and the origin of the underground water in our sea-provinces. 738.
- MOTIONS (On a decomposition of a continuous motion about a fixed point  $O$  of  $S$  into two continuous) about  $O$  of  $S_3$ 's. 716. Observation of Dr. E. JAHNKE. 831.
- MUCOUS MEMBRANE (The process of involution of the) of the uterus of *Tarsius spectrum* after parturition. 302.
- MUTATION of plants (Investigations of some Xanthine derivatives in connection with the internal). 203.
- MYOCARD (On the development of the) in Teleosts. 218.
- NITRATION (The) of Benzene fluoride. 659.
- NORTH-HOLLAND (Deep boulder-clay beds of a latter glacial period in). 340.
- NUMBERS (PLÜCKER'S) of a curve in  $S_4$ . 501.
- OCIMENE (On). 700.
- ONNES (H. KAMERLINGH). See KAMERLINGH ONNES (H.).
- OPTICAL METHOD of TYNDALL (Can the presence of the molecules in solutions be proved by application of the). 735.
- ORIENTATIC-PHENOMENA (Hysteretic). 597.
- ORIGIN (Facts leading to trace out the motion and the) of the underground water in our sea-provinces. 738.
- OSCULATING PLANE (On the position of the three points which a twisted curve has in common with its). 622.
- OUDEMANS (C. A. J. A.). *Exosporina Laricis* Oud. — A new microscopic fungus occurring on the Larch and very injurious to this tree. 498.  
 — and C. J. KONING. On a *Sclerotinia* hitherto unknown and injurious to the cultivation of tobacco (*Sclerotinia Nicotianae* OUD. et KONING). 48. Postscript. 85.
- OXYGEN and carbon dioxide (Isothermals of mixtures of). I. The calibration of manometer and piezometertubes. 532. II. The preparation of the mixtures and the compressibility at small densities. 541. III. The determination of isothermals between 60 and 140 atmospheres, and between  $-15^{\circ}$  C. and  $+60^{\circ}$  C. 554.

- IV. Isothermals of pure carbon dioxide between 25° C. and 60° C. and between 60 and 140 atmospheres. 565. V. Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide. 577. VI. Influence of gravitation on the phenomena in the neighbourhood of the plaitpoint for binary mixtures. 593.
- OXYGEN (Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of), and the comparison of them with those of pure carbon dioxide. 577.
- PANNEKOEK (A.). Some remarks on the reversibility of molecular motions. 42.
- PEKELHARING (C. A.) presents a paper of Dr. M. C. DEKHUYZEN and P. VERMAAT: "On the epithelium of the surface of the stomach." 30.
- presents a paper of Dr. R. O. HERZOG: "On the action of Fmulsin." 332.
- PENTACETATES (The mutual transformation of the two stereoisomeric) of *D*-glucose. 779.
- PERIODICITY (The) of solar phenomena and the corresponding periodicity in the variations of meteorological and earth-magnetic elements, explained by the dispersion of light. 270.
- PHASES (Theoretical consideration concerning boundary reactions which decline in two or more successive). 846.
- PHENOMENA of solidification (The) and transformation in the systems  $\text{NH}_4\text{NO}_3$ ,  $\text{AgNO}_3$  and  $\text{KNO}_3$ ,  $\text{AgNO}_3$ . 259.
- PHOCA VITULINA (The foetal membrane and the placenta of). 610.
- PHOSPHORUS (The action of) on hydrazine. 1.
- PHYLA (On the relationship of various invertebrate). 839.
- Physics. P. ZEEMAN and J. GEEST: "On the double refraction in a magnetic field near the components of a quadruplet." 19.
- A. PANNEKOEK: "Some remarks on the reversibility of molecular motions." 42.
- J. E. VERSCHAFFELT: "Contributions to the knowledge of VAN DER WAALS  $\psi$ -surface. VII. The equations of state and the  $\psi$ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components. (part 3). 59. (part 4). 115. VIII. The  $\psi$ -surface in the neighbourhood of a binary mixture which behaves as a pure substance. 649.
- J. D. VAN DER WAALS: "The liquid state and the equation of condition." 123.
- J. D. VAN DER WAALS: "The equilibrium between a solid body and a fluid phase, especially in the neighbourhood of the critical state." 230. 2nd part. 357.
- W. H. JULIUS: "The periodicity of solar phenomena and the corresponding periodicity in the variations of meteorological and earth-magnetic elements, explained by the dispersion of light." 270.
- J. P. KUENEN: "On the critical mixing-point of the two liquids." 387.
- G. VAN DIJK and J. KUNST: "A determination of the electrochemical equivalent of silver." 441.
- C. H. BRINKMAN: "The determination of the pressure with a closed airmanometer." 510.

- Physics.** W. H. KEESOM : "Isothermals of mixtures of oxygen and carbon dioxide. I. The calibration of manometer and piezometer tubes. 532. II. The preparation of the mixtures and the compressibility at small densities. 541. III. The determination of isothermals between 60 and 140 atmospheres, and between  $-15^{\circ}$  C. and  $+60^{\circ}$  C. 554. IV. Isothermals of pure carbon dioxide between  $25^{\circ}$  C. and  $60^{\circ}$  C. and between 60 and 140 atmospheres." 565. V. Isothermals of mixtures of the molecular compositions 0.1047 and 0.1994 of oxygen, and the comparison of them with those of pure carbon dioxide. 577. VI. Influence of gravitation on the phenomena in the neighbourhood of the plaitpoint for binary mixtures." 593.
- H. E. J. G. DU BOIS : "Hysteretic orientatic-phenomena." 597.
- H. KAMERLINGH ONNES and C. A. CROMMELIN : "On the measurement of very low temperatures. VI. Improvements of the protected thermoelements; a battery of standard-thermoelements and its use for thermoelectric determinations of temperature." 642.
- H. KAMERLINGH ONNES : "Methods and apparatus used in the cryogenic Laboratory. VI. The methylechloride circulation." 668.
- H. KAMERLINGH ONNES and H. HAPPEL : "The representation of the continuity of the liquid and gaseous conditions on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of GIBBS." 678.
- L. H. SIERTSEMA : "Investigation of a source of errors in measurements of magnetic rotations of the plane of polarisation in absorbing solutions." 760.
- PH. KOHNSTAMM : "On the equations of CLAUSIUS and VAN DER WAALS for the mean length of path and the number of collisions." 787.
- PH. KOHNSTAMM : "On VAN DER WAALS' equation of state." 794.
- Miss J. REUDLER : "Note on SYDNEY YOUNG's law of distillation." 807.
- H. A. LORENTZ : "Electromagnetic phenomena in a system moving with any velocity smaller than that of light." 809.
- Physiology.** M. C. DEKHUYZEN and P. VERMAAT : "On the epithelium of the surface of the stomach." 30.
- E. HEKMA : "On the liberation of trypsin from trypsin-zymogen." 34.
- J. K. A. WERTHEIM SALOMONSON : "A new law concerning the relation between stimulus and effect" (6<sup>th</sup> communication). 73.
- A. GORTER : "The cause of sleep." 86.
- W. EINTHOVEN : "The string galvanometer and the human electrocardiogram." 107.
- J. BOEKE : "On the development of the myocard in Teleosts." 218.
- G. VAN RIJNBEEK : "On the fact of sensible skin-areas dying away in a centripetal direction." 346.
- C. WINKLER and G. VAN RIJNBEEK : "Structure and function of the trunk-dermatoma." IV. 347.
- C. WINKLER and G. VAN RIJNBEEK : "Something concerning the growth of the lateral areas of the trunk-dermatomata on the caudal portion of the upper extremity." 392.
- J. K. A. WERTHEIM SALOMONSON : "On tactual after-images." 481.
- W. EINTHOVEN : "On some applications of the string-galvanometer." 707.

- PIEZOMETERTUBES (The calibration of manometer and). 532.
- PLACE (T.) presents a paper of Dr. J. BOEKE: "On the development of the myocard in Teleostis." 218.
- PLACENTA (The foetal membrane and the) of *Phoca vitulina*. 610.
- PLAINPOINT (Influence of gravitation on the phenomena in the neighbourhood of the) for binary mixtures. 593.
- PLANE OF POLARISATION (Investigation of a source of errors in measurements of magnetic rotations of the) in absorbing solutions. 760.
- PLANTS (Determination of the action of poisons on). 703.  
— (Investigations of some Xanthine derivatives in connection with the internal mutation of). 203.
- PLÜCKER'S numbers of a curve in  $S_4$ . 501.
- POINT  $O$  of  $S_4$  (On a decomposition of a continuous motion about a fixed) into two continuous motions about  $O$  of  $S_3$ 's. 716. Observation of Dr. E. JAHNKE. 831.  
— of  $S_4$  (Algebraic deduction of the decomposability of the continuous motion about a fixed) into those of two  $S_3$ 's. 832.
- POINTS (On the position of the three) which a twisted curve has in common with its osculating plane. 622.
- POISONS (Determination of the action of) on plants. 703.
- POLYTOPES (Centric decomposition of). 366.  
— (Regular projections of regular). 783.
- POTTER VAN LOON (J.) and A. F. HOLLEMAN. The transformation of benzidine. 262.
- PRESSURE (The determination of the) with a closed airmanometer. 510.  
— (Description of an apparatus for regulating the) when distilling under reduced pressure. 665.
- PROJECTIONS (Regular) of regular polytopes. 783.
- QUADRUPLET (On the double refraction in a magnetic field near the components of a). 19.
- RAKEN (H.). The transformation of diphenylnitrosamine into *p*-nitroso-diphenylamine and its velocity. 267.
- REARRANGEMENT (The BECKMANN); transformation of acetophenoxime into acetanilide and its velocity. 773.
- REARRANGEMENTS (On intramolecular). No. 5. C. L. JUNGUIS: "The mutual transformation of the two stereo-isomeric methyl-*d*-glucosides." 99. No. 6. H. RAKEN: "The transformation of diphenylnitrosamine into *p*-nitroso-diphenylamine and its velocity." 267. No. 7. C. A. LOBBY DE BRUYN and C. H. SLUITER: "The BECKMANN-rearrangement: transformation of acetophenoxime into acetanilide and its velocity." 773. No. 8. C. L. JUNGUIS: "The mutual transformation of the two stereoisomeric pentacetates of *d*-glucose." 779.
- REFRACTION (On the double) in a magnetic field near the components of a quadruplet. 19.
- REUDLER (J.). Note on SYDNEY YOUNG'S law of distillation. 807.
- REVERSIBILITY (Some remarks on the) of molecular motions. 42.

- ROMBURGH (P. VAN). On Ocimene. 700.
- Additive compounds of s. trinitrobenzene. 702.
- ROOTS (On the penetration into mercury of the) of freely floating germinating seeds. 182.
- ROOZEBOOM (H. W. BAKHUIS). See BAKHUIS ROOZEBOOM (H. W.).
- RUTTEN (JAN). Description of an apparatus for regulating the pressure when distilling under reduced pressure. 665.
- RIJNBEEK (G. VAN). On the fact of sensible skin-areas dying away in a centripetal direction. 346.
- and C. WINKLER. Structure and function of the trunk-dermatoma. IV. 347.
  - Something concerning the growth of the lateral areas of the trunkdermatomata on the caudal portion of the upper extremity. 392.
- SANDEBAKHUYZEN (E. F. VAN DE). Investigations of the errors of the tables of the moon of HANSEN-NEWCOMB for the years 1895—1902. 370. 2nd paper. 412. 422.
- presents a paper of C. SANDERS: "Contributions to the determination of geographical positions on the West-coast of Africa." II. 426.
- SANDERS (C.). Contributions to the determination of geographical positions on the West-coast of Africa. II. 426.
- SCHOOTE (P. H.) presents a paper of Dr. W. A. VERSLUYS: "The singularities of the focal curve of a curve in space." 17.
- Centric decomposition of polytopes. 366.
  - PLÜCKER's numbers of a curve in  $S_3$ . 501.
  - presents a paper of Dr. W. A. VERSLUYS: "The singularities of the focal curve of a plane general curve touching the line at infinity  $\sigma$  times and passing  $\epsilon$  times through each of the imaginary circle points at infinity." 621.
  - presents a paper of Dr. W. A. VERSLUYS: "On the position of the three points which a twisted curve has in common with its osculating plane." 622.
  - Regular projections of regular polytopes. 783.
- SCHUH (FRED.). An equation of reality for real and imaginary plane curves with higher singularities. 764.
- SCLEROTINIA (On a) hitherto unknown and injurious to the cultivation of tobacco (Sclerotinia Nicotianae OUD. et KONING). 48. Postscript. 85.
- SEA-PROVINCES (Facts leading to trace out the motion and the origin of the underground water in our). 738.
- SEEDS (On the penetration into mercury of the roots of freely floating germinating). 182.
- SERIES derived from the series  $\sum \frac{\mu(m)}{m}$ . 305.
- SIBOGA-EXPEDITION (On some of the results of the). 846.
- SHERTSEMA (L. H.). Investigation of a source of errors in measurements of magnetic rotations of the plane of polarisation in absorbing solutions. 760.
- SILVER (A determination of the electrochemical equivalent of). 441.
- SKEW CURVE (On complexes of rays in relation to a rational). 12.
- SKIN-AREAS (On the fact of sensible) dying away in a centripetal direction. 346.
- SLEEP (The cause of). 86.

- SLUITER (C. H.). The transformation of isonitrosoacetophenonsodium into sodium benzoate and hydrogen cyanide. 453.
- and C. A. LOBBY DE BRUYN. The BECKMANN-rearrangement; transformation of acetophenoxime into acetanilide and its velocity. 773.
- SMITS (A.). The course of the solubility curve in the region of critical temperatures of binary mixtures. 171. 2<sup>nd</sup> communication. 484.
- A contribution to the knowledge of the course of the decrease of the vapour tension for aqueous solutions. 628.
- and L. K. WOLFF. The velocity of transformation of carbon monoxide. II. 66.
- SODIUM (The electrolytic conductivity of solutions of) in mixtures of ethyl- or methyl-alcohol and water. 104.
- SODIUM BENZOATE (The transformation of isonitrosoacetophenonsodium into) and hydrogen cyanide. 453.
- SOLAR PHENOMENA (The periodicity of) and the corresponding periodicity in the variations of meteorological and earth-magnetic elements, explained by the dispersion of light. 270.
- SOLIDIFICATION (The phenomena of) and transformation in the systems  $\text{NH}_4\text{NO}_3$ ,  $\text{AgNO}_3$  and  $\text{KNO}_3$ ,  $\text{AgNO}_3$ . 259.
- SOLUBILITY CURVE (The course of the) in the region of critical temperatures of binary mixtures. 171. 2<sup>nd</sup> communication. 484.
- SOLUBILITY LINES (Abnormal) in binary mixtures owing to the existence of compounds in the solution. 456.
- SOLUTIONS (Absorption-compounds which may change into chemical compounds or). 368.
- (Changes of concentration in and crystallisation from) by centrifugal power. 846.
- (Investigation of a source of errors in measurements of magnetic rotations of the plane of polarisation in absorbing). 760.
- SOLVENT (Do the Ions carry the) with them in electrolysis. 97.
- SOURCE OF ERRORS (Investigation of a) in measurements of magnetic rotations of the plane of polarisation in absorbing solutions. 760.
- STANDARD-THERMOELEMENTS (A battery of) and its use for thermoelectric determinations of temperature. 642.
- STIMULUS and effect (A new law concerning the relation between). (6<sup>th</sup> communication). 73.
- STOK (J. P. VAN DER). Extract from the Report made by the committee for awarding the BUYS-BALLOT medal. 78.
- presents a paper of Dr. W. VAN BEMMELEN: "The daily field of magnetic disturbance." 313.
- STOMACH (On the epithelium of the surface of the). 30.
- STRAHL (HANS). The process of involution of the mucous membrane of the uterus of *Tarsius spectrum* after parturition. 302.
- STRING-GALVANOMETER (The) and the human electrocardiogram. 107.
- (On some applications of the). 707.
- SUBLIMATION LINES (The) of binary mixtures. 408.
- SUBSTITUTION (On the) of the core of Benzene. 735.

- SULPHUR and chlorine (The boiling-point curves of the system). 63.
- + chlorine (The meltingpoint lines of the system). 599.
- ψ-SURFACE (Contributions to the knowledge of VAN DER WAALS). VII. The equations of state and the ψ-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components (part 3). 59. (part 4). 115. VIII. The ψ-surface in the neighbourhood of a binary mixture which behaves as a pure substance. 649.
- SYDNEY YOUNG's law of distillation (Note on). 807.
- SYMMETRY of position (Crystallographic and molecular) isomeric benzene derivatives. 406.
- sulphur and chlorine (The boiling-point curves of the). 63.
- SYSTEM bromine + iodine (The). 331.
- sulphur + chlorine (The meltingpoint lines of the). 599.
- (Electromagnetic phenomena in a) moving with any velocity smaller than that of light. 809.
- SYSTEMS  $\text{NH}_4\text{NO}_3$ ,  $\text{AgNO}_3$  and  $\text{KNO}_3$ ,  $\text{AgNO}_3$  (The phenomena of solidification and transformation in the). 259.
- of conics (On) belonging to involutions on rational curves. 505.
- TABLES OF THE MOON (Investigations of the errors of the) of HANSEN-NEWCOMB for the years 1895—1902. 379. 2nd paper. 412. 422.
- TARSIVS spectrum (The process of involution of the mucous membrane of the uterus of) after parturition. 302.
- TELEOSTS (On the development of the myocard in). 218.
- TEMPERATURES (On the measurement of very low). VI. Improvements of the protected thermoelements; a battery of standard-thermoelements and its use of thermoelectric determinations of temperature. 642.
- TENSION THEORY (A quantitative research concerning BAEYER's.) 410.
- Terrestrial Magnetism.** W. VAN BEMMELEN: "The daily field of magnetic disturbance." 313.
- THERMOELEMENTS (Improvements of the protected); a battery of standard-thermoelements and its use for thermoelectric determinations of temperature. 642.
- TOBACCO (On a Sclerotinia hitherto unknown and injurious to the cultivation of) (Sclerotinia Nicotianae Oud. et Koning). 48. Postscript. 85.
- TRANSFORMATION of acetophenoxime into acetanilide and its velocity. 773.
- (The phenomena of solidification and) in the systems  $\text{NH}_4\text{NO}_3$ ,  $\text{AgNO}_3$  and  $\text{KNO}_3$ ,  $\text{AgNO}_3$ . 259.
- (The) of benzidine. 262.
- (The) of diphenylnitrosamine into *p*-nitroso-diphenylamine and its velocity. 267.
- (The) of isonitrosoacetophenonsodium into sodium benzoate and hydrogen cyanide. 453.
- (The mutual) of the two stereo-isomeric methyl-*d*-glucosides. 99.
- (The mutual) of the two stereo-isomeric pentacetates of *d*-glucose. 779.
- (On symmetric) of  $S_4$  in connection with  $S_7$  and  $S_7$ . 785.

- TRINITROBENZENE (Additive compounds of s.). 702.
- TRUNKDERMATOMATA (Something concerning the growth of the lateral areas of the) on the caudal portion of the upper extremity. 392.  
— (Structure and function of the). IV. 347.
- TRYPSIN (On the liberation of) from trypsin-zymogen. 34.
- TWISTED CURVE (On the position of the three points which a) has in common with its osculating plane. 622.
- TYMSTRA BZ. (s.). The electrolytic conductivity of solutions of sodium in mixtures of ethyl- or methylalcohol and water. 104.
- TYNDALL (Can the presence of the molecules in solutions be proved by application of the optical method of). 735.
- UTERUS of *Tarsius spectrum* (The process of involution of the mucous membrane of the) after parturition. 302.
- VAPOUR TENSION (A contribution to the knowledge of the course of the) for aqueous solutions. 628.
- Vegetable Physiology.** TH. WEEVERS and Mrs. C. J. WEEVERS—DE GRAAFF: "Investigations of some Xanthine derivatives in connection with the internal mutations of plants." 203.
- VELOCITY (Electromagnetic phenomena in a system moving with any) smaller than that of light. 809.  
— of transformation (The) of carbon monoxide. II. 66.
- VERMAAT (P.) and M. C. DEKHUYZEN. On the epithelium of the surface of the stomach. 30.
- VERSCHAFFELT (E.). Determination of the action of poisons on plants. 703.
- VERSCHAFFELT (J. E.). Contributions to the knowledge of VAN DER WAALS  $\psi$ -surface. VII. The equations of state and the  $\psi$ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components (part 3). 59. (part 4). 115. VIII. The  $\psi$ -surface in the neighbourhood of a binary mixture which behaves as a pure substance. 649.
- VERSLUYS (W. A.). The singularities of the focal curve of a curve in space. 17.  
— The singularities of the focal curve of a plane general curve touching the line at infinity  $\sigma$  times and passing  $\varepsilon$  times through each of the imaginary circle points at infinity. 621.  
— On the position of the three points which a twisted curve has in common with its osculating plane. 622.
- VISSER (A. W.). Enzymactions considered as equilibria in a homogenous system. 605.
- VOERMAN (G. L.) and A. F. HOLLEMAN. A quantitative research concerning BAEYER's tension theory. 410.
- VRIES (J. DE). On complexes of rays in relation to a rational skew curve. 12.  
— The harmonic curves belonging to a given plane cubic curve. 197.  
— On systems of conics belonging to involutions on rational curves. 505.  
— Fundamental involutions on rational curves of order five. 508.

- W A A L S (V A N D E R) (On the equations of CLAUSIUS and) for the mean length of path and the number of collisions. 787.
- $\psi$ -surface (Contributions to the knowledge of). VII. The equations of state and the  $\psi$ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components (part 3). 59. (part 4). 115. VIII. The  $\psi$ -surface in the neighbourhood of a binary mixture which behaves as a pure substance. 649.
  - equation of state (On). 794.
- W A A L S (J. D. V A N D E R). The liquid state and the equation of condition. 123.
- The equilibrium between a solid body and a fluid phase, especially in the neighbourhood of the critical state. 230. 2nd part. 357.
  - presents a paper of Prof. J. P. KUENEN: "On the critical mixing-point of the two liquids." 387.
  - presents a paper of C. H. BRINKMAN: "The determination of the pressure with a closed airmanometer." 510.
  - presents a paper of Prof. H. E. J. G. DU BOIS: "Hysteretic orientatic-phenomena". 597.
  - presents a paper of Dr. PH. KOHNSTAMM: "On the equations of CLAUSIUS and VAN DER WAALS for the mean length of path and the number of collisions." 787.
  - presents a paper of Dr. PH. KOHNSTAMM: "On VAN DER WAALS' equation of state." 794.
  - presents a paper of Miss J. REUDLER: "Note on SYDNEY YOUNG's law of distillation." 807.
- W A T E R (Facts leading to trace out the motion and the origin of the underground) in our sea-provinces. 738.
- (The electrolytic conductivity of solutions of sodium in mixtures of ethyl- or methylalcohol and). 104.
- W E B E R (M A X). On some of the results of the Siboga-Expedition. 846.
- W E E V E R S (T H.) and Mrs. C. J. W E E V E R S—D E G R A A F F. Investigations of some Xanthine derivatives in connection with the internal mutation of plants. 203.
- W E N T (F. A. F. C.) presents a paper of Dr. G. GRIJNS: "The Ascus-form of *Aspergillus fumigatus* Fresenius." 312.
- W E R T H E I M S A L O M O N S O N (J. K. A.). A new law concerning the relation between stimulus and effect. 73.
- On tactual after-images. 481.
- W I L L I O T (v.). — Extract of a letter of — on the work of D. BIERENS DE HAAN: "Théorie, propriétés, formules de transformation et méthodes d'évaluation des intégrales définies." 226.
- W I N D (C. H.). Extract from the Report made by the Committee for awarding the BUYS—BALLOT medal. 78.
- W I N K L E R (C.) presents a paper of Prof. J. K. A. WERTHEIM SALOMONSON: "A new law concerning the relation between stimulus and effect." (6th Communication). 73.

- WINKLER (C.) presents a paper of Dr. A. GORTER: "The cause of sleep." 86.
- presents a paper of Dr. G. VAN RIJNBERK: "On the fact of sensible skin areas dying away in a centripetal direction." 346.
- presents a paper of Prof. J. K. A. WERTHEIM SALOMONSON: "On tactual after-images." 481.
- and G. VAN RIJNBERK. Structure and function of the trunk-dermatoma. IV. 347.
- Something concerning the growth of the lateral areas of the trunk-dermatomata on the caudal portion of the upper extremity. 392.
- WOLFF (L. K.) and C. A. LOBRY DE BRUYN. Can the presence of the molecules in solutions be proved by application of the optical method of TYNDALL. 735.
- WOLFF (L. K.) and A. SMITS. The velocity of transformation of carbon monoxide. II. 66.
- XANTHINE DERIVATIVES (Investigations of some) in connection with the internal mutation of plants. 203.
- ZEEEMAN (P.). Extract from the Report made by the committee for awarding the BUYS—BALLOT medal. 78.
- and J. GEEST. On the double refraction in a magnetic field near the components of a quadruplet. 19.
- Zoology.** HANS STRAHL: "The process of involution of the mucous membrane of the uterus of *Tarsius spectrum* after parturition." 302.
- A. A. W. HUBRECHT: "On the relationship of various invertebrate phyla." 839
- MAX WEBER: "On some of the results of the Siboga-Expedition." 846.
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